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CONTENTS

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THE INTERACTION BETWEEN RUBBER AND LIQUIDS. VII. THE HEATS AND ENTROPIES OF DILUTION OF NATURAL RUBBER BY VARIOUS LIQUIDS *

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INTRODUCTION

Considerable progress has been made in interpreting the properties of polymer solutions and gels in the light of statistical calculations of the entropy of mixing of polymers with liquids[1]. The basis of most of these applications has been the assumption that the Gibbs free energy of dilution ΔG_0 at such a mixture by the liquid is expressible in terms of the entropy of dilution ΔS_0, as calculated statistically on the assumption of random mixing, and a heat of dilution ΔH_0 proportional to the square of the volume fraction v_r of the polymer. Huggins has shown that a wide variety of thermodynamic data can be represented in this way; the present paper includes a more sensitive test of the validity of the assumption.

Free energies of dilution of polymer solutions have been calculated[2] from data on vapor pressure, osmotic pressure, swelling pressure, and freezing-point depression. Corresponding values for the heats of dilution are almost entirely lacking, and it is therefore impossible to check whether the quantity employed to relate the theoretical entropy to the experimental free energy is equal to the heat of dilution, or whether it contains also an empirical correction factor. The direct measurement of heats of dilution for polymer systems is exceedingly difficult; a new attempt to do so for mixtures of natural rubber + benzene is now in progress. Here we present estimates of the heats of mixing of natural rubber with a number of liquids, based on calorimetric measurements of the heats of mixing of low-molecular liquid homologs of rubber with the same liquids, and of the entropies of mixing obtained by combining these with vapor-pressure data.

HEAT AND VOLUME CHANGES ON MIXING DIHYDROMYRCENE AND SQUALENE WITH OTHER LIQUIDS

A quantity of dihydromyrcene and a much smaller amount of squalene were made available to us by E. H. Farmer, to whom our thanks are due. These substances contain, respectively, two and six isoprene units per molecule, and may thus be regarded as very low-molecular homologs of natural rubber. The heats of mixing of dihydromyrcene with a series of liquids were measured in the calorimeter shown in Figure 1. To conserve materials it was necessary to work with relatively small volumes of liquids (not more than 10 cc. dihydromyrcene for the whole series of measurements on each liquid). The heat absorption to be measured in a typical mixing was thus of the order of 1 calorie. Attempts to do this in a small vacuum-jacketted calorimeter of small heat

capacity were rendered inaccurate by relatively large heat losses, and the arrangement shown was finally adopted. It consisted of a thermostatted vacuum vessel almost filled with water, in which were suspended two coaxial bulbs, the tube of the inner bulb being a close fit into the outer so as to minimize loss by evaporation. The liquids A and B were in the outer and inner bulbs, respectively, the lower end of the latter being sealed by a pool of mercury. Mixing of the two liquids was accomplished by raising the inner bulb out of the mercury and rotating it so that the liquid was stirred by the vanes attached to the inner bulb. Several samples of B could be added successively wjthout
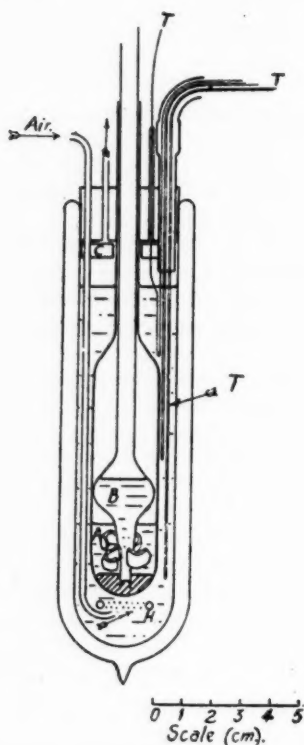
Fig. 1.—Calorimeter.

removing the calorimeter from the thermostat, the inner bulb being completely emptied each time by passing a gentle stream of nitrogen through it. The water in the calorimeter was stirred by a slow stream of air presaturated with water vapor. A layer of cork, C, was found necessary to prevent water splashing through the exit tube. The temperature change was measured by ten copper-eureka thermocouples, T, in series, arranged at different levels, with cold junctions in a second vacuum vessel also filled with water, and contained in the same thermostat; the connecting leads passed through a short length of lead tubing. The heater H was of about 10 ohms resistance, and permitted small measured quantities of energy to be introduced to determine the heat capacity. This was approximately 65 calories, so the temperature change to

be measured was of the order of a hundredth of a degree, and the thermo-electric e.m.f. a few microvolts. This was measured directly by means of a Tinsley taut suspension galvanometer, of resistance 9.5 ohms and sensitivity 180 mm. per microampere. The overall sensitivity (maximum 5 meters per degree) was determined by calibrating against Beckmann thermometers, the, galvanometer deflection being very nearly proportional to the temperature difference between the hot and cold junctions.

To make the heat interchange with the surroundings during an experiment small compared with the quantity to be measured, it was necessary that both hot and cold junctions should be very near to the thermostat temperature[3]. To ensure this, it was found desirable to check the cold junction temperature before and during an experiment by a Beckmann thermometer, and to leave the calorimeter in the thermostat overnight before making the first addition. Subsequent additions could be made after an interval of 1 to 2 hours. Under these conditions, the correction for heat interchange with the surroundings was small, and the temperature change on mixing was nearly that calculated from the maximum galvanometer deflection.

A typical series of measurements of the heat of mixing of the two liquids was performed in two parts. In the first, 5 cc. of liquid A in the outer bulb was diluted with four successive additions of liquid B, until the mixture contained approximately equal volumes of A and B. The procedure was then repeated, with the liquids interchanged. The heat absorptions measured were used to calculate the heat of mixing ΔH^m of v_0 cc. of liquid A with $(1 - v_0)$ cc. of liquid B; results obtained in this way for CS_2 + dihydromyrcene are shown in Figure 2. In accordance with the usage of earlier papers the volume
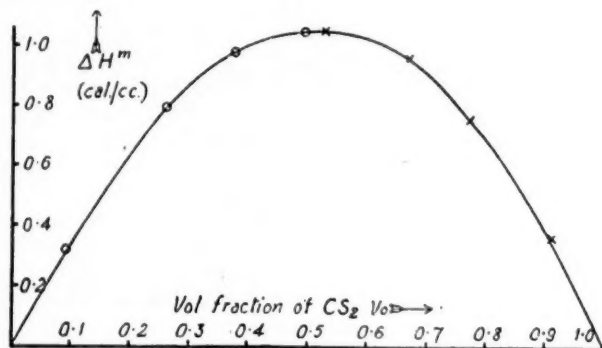
Fig. 2.—Heat of mixing of carbon disulfide and dihydromyrcene.

fraction of dihydromyrcene (regarded as "rubber") is written v_r; that of the other liquid v_0. Points in the two halves of the experiment are differently indicated, and it will be noted that all lie on a smooth, almost parabolic curve. This curve would be exactly parabolic if Hildebrand's expression[4] for the heat of mixing was obeyed:

$$\Delta H^m = \alpha v_0 v_r \tag{1}$$

The deviation from this form can be represented most readily by employing each experimental point to calculate a value of α; the results for a series of

liquids are shown in Figure 3. It is evident that Equation (1) is obeyed with considerable accuracy by most of the liquids examined, only acetone and chloroform showing large deviations. There appears to be a real, though small, deviation in the carbon-disulfide data, although the extreme points are less accurate than the remainder.
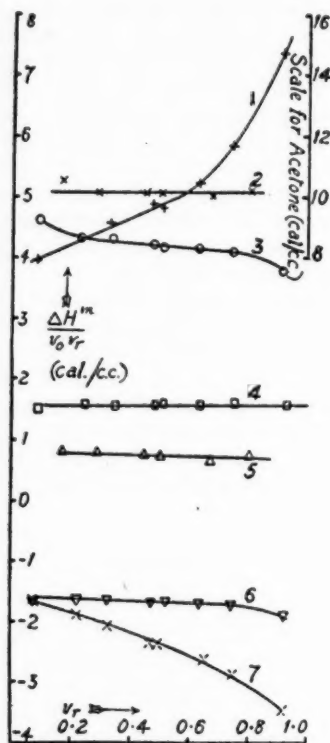
FIG. 3.—Heats of mixing of liquids with dihydromyrcene

1. Acetone
2. Benzene
3. Carbon disulfide
4. Toluene
5. Heptane
6. Carbon tetrachloride
7. Chloroform

The constant α is given, according to Hildebrand's theory by:

$$\alpha = (\sqrt{e_0} - \sqrt{e_r})^2 \qquad (1)$$

where e_0 and e_r are the cohesive energy densities of the liquid and of dihydromyrcene; α should thus always be positive, so that (2) evidently breaks down for chloroform and carbon tetrachloride. By comparison with other hydrocarbons we may estimate $\sqrt{e_r}$ for dihydromyrcene as 7.4_2 (cal. per cc.)$^{\frac{1}{2}}$, for squalene as 7.7_8 (cal. per cc.)$^{\frac{1}{2}}$ while the value for natural rubber has been previously estimated[5] as 7.9_8. In Table I, values of α calculated from (2) are compared with the experimental values, and it is evident that, while there is a rough agreement as to order of magnitude for benzene, toluene, heptane, carbon disulfide and acetone, the halogenated hydrocarbons fall completely out of line.

It has been suggested[6] that the general source of disagreement between calculated and experimental heats of mixing of liquids arises from the failure of the assumption involved in the derivation of Equation (2) that there is no volume change on mixing. To test the importance of this factor in the present case, the volume changes on mixing were measured in a simple modification of the apparatus described by Hildebrand and Carter[7]. It consisted of a U-tube of total volume about 7 cc., the upper parts of the two limbs being of capillary tubing, closed at the outer ends by stoppers. The tube was filled with 3 cc. of mercury plus 2 cc. of each liquid under examination, and thermostatted, the mercury forming a seal between the two liquids. After reading the liquid levels in the capillaries, the two liquids were mixed by allowing the mercury to flow from limb to limb and the levels again noted. The expansions observed (ΔV^m cc. per cc. of total liquid), are given in Table I, expressed as $100 \Delta V^m / v_0 v_r$,

TABLE I

HEAT AND VOLUME CHANGES IN DIHYDROMYRCENE MIXTURES

Liquid	$\sqrt{\epsilon_0}$ (cal. per cc.)$^{\frac{1}{2}}$	α(cal. per cc.) calculated	α(cal. per cc.) observed	$100 \dfrac{\Delta V^m}{v_0 v_r}$ (cc.)
Benzene	9.1_8	3.1_0	5.1	1.5
Toluene	9.0_2	2.5_6	1.60	0.2
Heptane	7.5_0	0.0_1	0.7_0	-0.4
CS₂ Carbon disulfide	10.0_5	6.9	4.2	1.2
Carbon tetrachloride	8.5_5	1.2_8	-1.7	-0.3
Acetone	9.7_7	5.5	8 to 16	0.4
Chloroform	9.3_0	3.5	-1.6 to -3.5	0.2

which is reproducible to ± 0.2 cc. The energy required to compress the mixture isothermally to the volume it would have if mixing occurred without change of volume is approximately $T\alpha_v \Delta V^m / 41.3\beta$ cal., where $\alpha_v(\deg.^{-1})$, $\beta(\text{at}_m{}^{-1})$ are the coefficients of cubical expansion and compressibility of the mixture. For most liquids at room temperature $T\alpha_v / 41.3\beta \approx 100$ cal. per cc., so the last column is approximately equal, numerically, to the contribution to the heat of mixing from the work done against the intermolecular forces in the observed expansion. This contribution is by no means negligible for benzene and carbon disulfide, but the lack of correlation between the last two columns shows that it does not account quantitatively for the discrepancy between the calculated and observed values of α. In view of this conclusion, it was not considered worthwhile to investigate the constancy of the function $\Delta V^m / v_0 v_r$.

ESTIMATION OF HEATS OF DILUTION OF RUBBER FROM CALORIMETRIC DATA

To obtain the heat of dilution ΔH_0, we rewrite Equation (1) to give the heat absorbed ΔH, on mixing N_0 moles of liquid (molar volume V_0) with N_r moles of rubber (molar volume V_r) in the form:

$$\Delta H = \frac{\alpha N_0 N_r V_0 V_r}{N_0 V_0 + N_r V_r} \tag{1'}$$

and differentiate, to obtain

$$\Delta H_0 \equiv \left(\frac{\partial \Delta H}{\partial N_0} \right)_{N_r} \tag{2}$$

If α is constant, the result is:

$$\Delta H_0/v_r^2 = \alpha V_0 \qquad (3)$$

If α is not constant, we may still express the experimental results in terms of α, and it may then be shown that:

$$\frac{\Delta H_0}{v_r^2} = V_0\left(\alpha - v_0\frac{\partial\alpha}{\partial v_r}\right) \qquad (4)$$

Using values of $\partial\alpha/\partial v_r$ from the smoothed curves of Figure 3, we thus obtain $\Delta H_0/v_r^2$ as functions of v_r for dihydromyrcene in acetone and chloroform; for the other liquids (3) may be used with sufficient accuracy.

We have now to consider the relation between the heats of dilution of dihydromyrcene and of rubber by the same liquid. If we denote the respective "constants" of Equation (1) by α_d, α_r, (2) gives:

$$\alpha_d = (\sqrt{e_0} - 7.42)^2; \qquad \alpha_r = (\sqrt{e_0} - 7.98)^2,$$

whence:

$$\alpha_d - \alpha_r = 1.12(\sqrt{e_0} - 7.70). \qquad (5)$$

This equation should be true provided that the difference between the heats of dilution of dihydromyrcene and rubber can be represented completely by the difference of cohesive energy density, i.e., provided that the factors responsible for the failure of Equation (2) are equally operative in both cases. This is clearly a plausible assumption, and one would expect (5) to hold much more closely than (2). A limited test of its validity has been made by comparing the heats of mixing of benzene and heptane with dihydromyrcene and squalene. Denoting the constant of mixtures with the latter by α_s, equation (5) should be replaced by:

$$\alpha_d - \alpha_s = 0.72\,(\sqrt{e_0} - 7.60) \qquad (5')$$
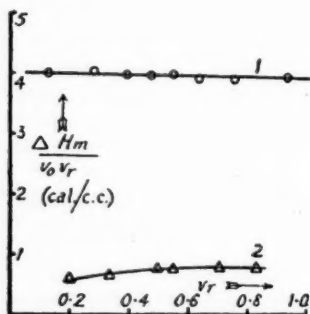
FIG. 4.—Heats of mixing of squalene with benzene (1), heptane (2).

The experimental data for the squalene mixtures are given in Figure 4, which shows Equation (1) to be very well obeyed. Table II shows that the observed and calculated values of $(\alpha_d - \alpha_s)$ are in excellent agreement:

Values of $\alpha_r V_0$ have therefore been computed by using the experimental values of α_d and values of $(\alpha_d - \alpha_r)$ calculated from Equation (5) giving:

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TABLE II

HEATS OF MIXING WITH SQUALENE AND DIHYDROMYRCENE

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Liquid	α_d	α_s	$\alpha_d - \alpha_s$ (observed)	$\alpha_d - \alpha_s$ (calculated)
Benzene	5.1	3.9_5	1.1_5	1.1_3
Heptane	0.65 to 0.8	0.8 to 0.7	$\pm 0.1_5$	0.07

For acetone and chloroform, combination of (4) and (5) gives:

$$\Delta H_0 / V_0 v_r^2 = \alpha_d - v_0 \partial \alpha_d / \partial v_r - 1.12 (\sqrt{e_0} - 7.70) \qquad (6)$$

Values of $\alpha H_0 / v_r^2$ plotted in Figure 5 were calculated from this expression. These results (Table III and Figure 5) constitute our estimates of the heats of dilution of natural rubber by the seven liquids concerned.
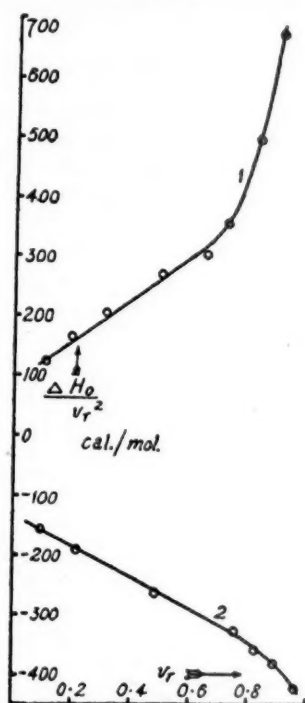
FIG. 5.—Estimated heat of dilution of natural rubber by: (1) acetone, (2) CHCl₃.

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TABLE III

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Liquid	$\alpha_r V_0 = \Delta H_0 / v_r^2$ (cal. per mole)
Benzene	310
Toluene	15
Heptane	135
Carbon disulfide	95
Carbon tetrachloride	-255

One rather puzzling feature is the apparent constancy of $\Delta H_0 / v_r^2$ for most of the liquids, since the number of contacts between rubber and liquid depend

on their relative molecular surfaces, which are not proportional to the volume fractions, except in the artificial case of infinite coördination number[8]. It is true that the constancy has only been proved experimentally for mixtures with dihydromyrcene and squalene, but the case of benzene + squalene affords a very striking example of the disagreement between theory and experiment; according to Orr's calculations[9] the value of $\Delta H_0/v_r^2$ at $v_r = 0$ should be only about one-half of that at $v_r = 1$. The origin of the discrepancy remains obscure, but these experimental results, so far as they go, support the usual practice of assuming $\Delta H_0 \propto v_r^2$ for polymer + liquid, as well as for mixtures of two liquids.

The heat of dilution obtained for benzene does not agree with our direct estimate reported earlier[10], according to which $\Delta H_0/v_r^2$ varies from 160 cal. per mole at $v_r = 1$ to 60 cal. per mole at $v_r = 0$; we wish to defer comment on this until further work on benzene, now in progress, is completed.

ESTIMATION OF ENTROPIES OF DILUTION

The free energy of dilution of natural rubber by each of these liquids has been calculated from the available vapor-pressure data, and combined with the above thermal measurements to give an estimate of the entropy of dilution. The results are shown in Figures 6 and 7, in which $\Delta S_0/v_r^2$ is plotted against v_r,
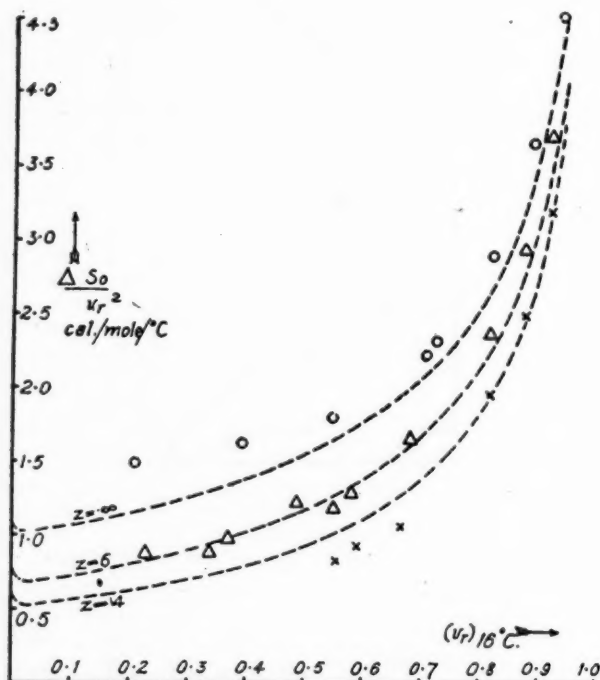
FIG. 6.—Entropy of dilution of natural rubber by hydrocarbons.

O Benzene at 25° C[13]   Δ Heptane at 40° C[14]   X Toluene at 25° C[15]
Dotted curves calculated from Equation (7).
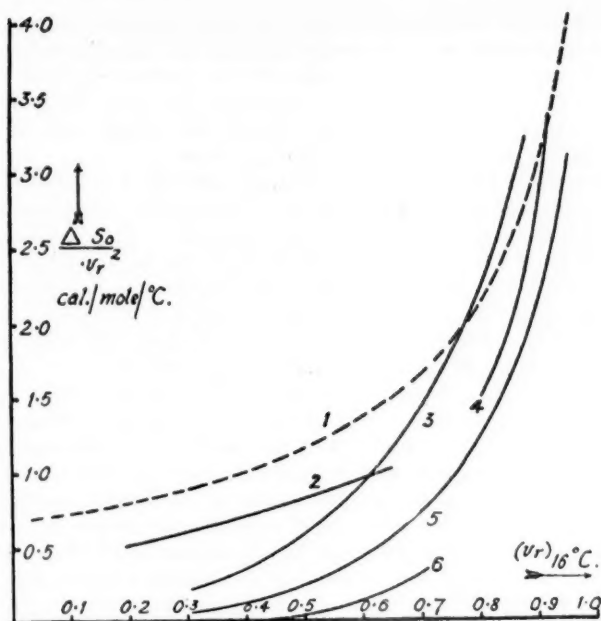
Fɪɢ. 7.—Entropy of dilution of natural rubber by polar liquids.

Curve 1. Theoretical ($Z = 6$).   Curve 4. Acetone at 35° C[18]
2. Carbon disulfide at 25° C[17]   5. Chloroform at 35° C[18]
3. Carbon tetrachloride at 35° C[18]   6. Chloroform at 25° C[18]

and compared with the theoretical value obtained from Miller's equation[11]:

$$\Delta S_0 = -R\left[\ln(1 - v_r) - \frac{Z}{2}\ln\left(1 - \frac{2v_r}{Z}\right)\right] \tag{7}$$

In Figure 6 curves are shown for three values of the coördination number Z, viz., 4, 6, ∞. With $Z = \infty$, (7) reduces to Flory's expression[12]:

$$\Delta S_0 = -R\left[\ln(1 - v_r) + v_r\right] \tag{8}$$

It is easily shown from (7) that:

$$\left(\frac{\Delta S_0}{v_r^2}\right) = \left(\frac{\Delta S_0}{v_r^2}\right)_{Z=\infty} - \frac{R}{Z}\left(1 + \frac{4}{3Z}\cdot v_r + \frac{2}{Z^2}\cdot v_r^2 + \cdots\right) \tag{9}$$

so plots of $\Delta S_0/v_r^2 \sim v_r$ for different values of Z are nearly superposable by adding suitable constants. Huggins[16] has shown that a very wide range of thermodynamic data (including that used here) can be represented by an equation of the form:

$$-\frac{\Delta G_0}{Tv_r^2} = \left(\frac{\Delta S_0}{v_r^2}\right)_{Z=\infty} - \frac{\mu}{RT} \tag{10}$$

where μ is a constant. Now, for those liquids for which $\Delta H_0 = \alpha_r V_0 v_r^2$ we have also:

$$-\frac{\Delta G_0}{Tv_r^2} = \frac{\Delta S_0}{v_r^2} - \frac{\alpha_r V_0}{T} \tag{11}$$

Huggins' observation thus requires that for these liquids the entropy curves should be either identical or at least superposable by adding suitable constants. This is nearly true in most cases, although the present method of plotting provides a much more severe test of Equation (10) than that employed by Huggins. If Equation (10) holds for liquids for which $\Delta H_0 \neq \alpha_r V_0 v_r^2$, it follows that $\Delta S_0/v_r^2$ cannot be of the standard form.

It is evident from Figures 6 and 7 that our estimated entropies of dilution, although generally of the expected form, do not agree quantitatively either among themselves or with the theoretical equation. It is unlikely that the free energies deduced from vapor pressure data can be seriously in error for $v_r > 0.5$, but the lower points are much less certain. Some part at least of the disagreement may arise from errors in the heats of dilution; this cannot at present be checked. Discussion of the origin of these different entropies of dilution must therefore be somewhat tentative at present.

The first point to be noted is that Equation (7) was deduced on the assumption of random mixing, so it can only be expected to apply accurately to athermal mixtures. The nearest approach to this condition is provided by toluene, heptane and carbon disulfide, and it is satisfactory to note that these three liquids give entropy curves in fair agreement with theory, assuming low coördination numbers (4 to 6). There is, of course, no reason to suppose that the coördination number will be the same for all mixtures of rubber + liquid, or even that it will necessarily be independent of concentration in any particular mixture. The effect of finite heats of mixing on the entropy of dilution has been estimated by Orr[9], and shown to be small for heats of mixing of the order found experimentally for most of the liquids with which we have worked, the only possible exception being acetone. The effect vanishes for $Z = \infty$, and for finite values of Z is positive at low v_r, negative at high. Using Orr's equation, the theoretical entropy of dilution of rubber by benzene, taking $N_w = 310$ cal.; $Z = 6$ is 2.08 cal./mole/°C at $v_r = 0.8$, which is almost identical with the value calculated for athermal mixing. The high entropy found experimentally for benzene appears to be a specific effect, and is probably due to the fact that this liquid is known from other evidence to be rather highly ordered[19], due no doubt to a tendency for the flat molecules to pack with the planes of adjacent molecules parallel. The very large expansion found on mixing with dihydromyrcene (Table I) is almost certainly connected with the breakdown of this ordered arrangement.

Acetone is an example of a liquid possessing a rather large heat of mixing with rubber, the two materials being only partially miscible. The tendency towards separation into two phases is shown by the rapid fall of both $\Delta H_0/T v_r^2$ and $\Delta S_0/v_r^2$ as the acetone content is increased, indicative of increasingly nonrandom mixing, although in the direction indicated by Orr's analysis, both effects are considerably greater than would be given by the theory. Taking $N_w = 1000$ cal., $Z = 6$, the calculated values at $v_r = 0.8$ are $\Delta H_0/v_r^2 = 680$ cal. per mole; $\Delta S_0/v_r^2 = 1.86$ cal./mole/°C. The maximum imbibition of acetone by rubber at 35° C should be only about 8 per cent by volume, compared with the experimental value of approximately 20 per cent. It is evident, therefore, that neither the crude theory, as developed by Flory and Huggins, nor Orr's refinement of it, applies quantitatively to this system.

Carbon tetrachloride and chloroform present a different kind of departure from the simple theory; the entropy of mixing is again small, but for these liquids ΔH_0 is negative, indicating a tendency towards complex formation

between the liquid and rubber. The very small entropies of dilution at low liquid concentrations affords further evidence of order in the mixture, associated with complex formation.

THERMODYNAMICS OF THE SYSTEM RUBBER + METHYL ALCOHOL

The evidence presented above shows that, although the statistical thermodynamic theory of polymer solutions holds reasonably well for normal mixtures, it is less satisfactory when the heat of mixing is large.   To test the usefulness of the present theories in an extreme case, we have studied the thermodynamic properties of mixtures of rubber + methyl alcohol.   Only about 2 per cent of methyl alcohol is imbibed by rubber at room temperature, so that a very limited concentration range is available for study.   Vapor pressures were measured at 25° and 35° C by a method previously described[13] and used to calculate the free energy and heat of dilution.   The results are shown in Figure 8, from which the following points may be noted.
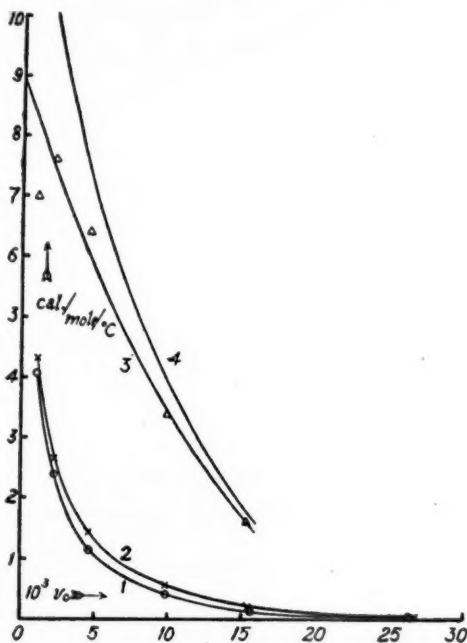
Fig. 8.—Thermodynamic functions for the system natural rubber + methyl alcohol.

(1) $-\dfrac{\Delta G_0}{T v_r^2}$ at 25° C.

(2) $-\dfrac{\Delta G_0}{T v_r^2}$ at 35° C.

(3) $\dfrac{\Delta H_0}{T v_r^2}$ at 30° C from (1) and (2).

(4) $\dfrac{\Delta S_0}{v_r^2}$ at 30° C from (1), (2) and (3).

(1) $\Delta H_0/v_r^2$ falls very rapidly as the alcohol content of the mixture increases.   This behavior is paralleled by the heats of solution in alcohols in low

molecular hydrocarbons[20], and must be ascribed to the almost complete association of alcohols except in the most dilute solution. The very large heat of dilution as $v_0 \to 0$ represents the energy of the hydrogen bonds, and is of the same order for methyl alcohol in rubber as for a range of alcohols in hexane and benzene.

(2) ΔS_0 is very much less than its theoretical value, except at very small v_0, and it is evident that mixing is far from random.

(3) These deviations are far larger than would be expected on the basis of Orr's calculation of the effect of a heat of mixing[9]. The discrepancy is not surprising, since the theory does not make allowance for association, which must in this case be the dominating cause of irregularity. Figure 9 shows the
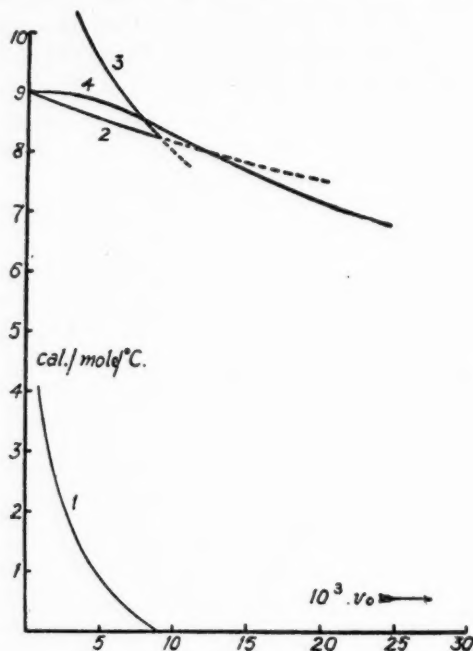
Fig. 9.—Theoretical thermodynamic functions for rubber and methyl alcohol at 30° C.

Curve 1. $\left. -\dfrac{\Delta G_0}{Tv_r{}^2} \right\}$

2. $\dfrac{\Delta H_0}{Tv_r{}^2}$ $\Biggr\}$ Theoretical for $\begin{cases} Z = 6. \\ N_w = 2.72 \text{ k. cal.} \end{cases}$

3. $\dfrac{\Delta S_0}{v_r{}^2}$

4. $\left(\dfrac{\Delta G_0}{Tv_r{}^2}\right)_{\text{expt.}} + \left(\dfrac{\Delta S_0}{v_r{}^2}\right)$ theoretical for $\begin{cases} \Delta H_0 = 0. \\ Z = 6. \end{cases}$

thermodynamic functions calculated from Orr's equation, assuming $Z = 6$, with the observed heat of dilution extrapolated to $v_0 = 0$. They lead to a predicted maximum imbibition of methyl alcohol at 30° C of $v_0 = 0.0088$, which is the same as that calculated from the entropy of random mixing with $\Delta H_0/v_r{}^2$ constant. The experimental value is some three times higher, a discrepancy very similar to that found for acetone. At the same time, curve 4

of Figure 9 shows that Huggins' Equation (10) is still quite a good approximation, the "consant" μ varying by no more than 25 per cent over the available concentration range. Over most of this range, however, it is not even approximately related to the heat of dilution, and it is clear that μ will be temperature dependent.

CONCLUSIONS

The statistical thermodynamic theory of polymer solutions is confirmed as a valid and useful first approximation. In general, the free energy of dilution can be expressed with considerable accuracy as the difference between an "apparent heat of dilution", proportional to v_r^2, and T times the entropy of dilution calculated for random mixing. The identification of these two terms as the true heat and entropy of dilution is not generally correct, both being subject to considerable variations arising from the existence of order in the components or in the mixture. These variations, whose effects on the free energy nearly cancel, are in the direction to be expected from Orr's analysis of the effect of a finite heat of mixing, but may be considerably larger. The present theory fails most seriously in the estimation of (1) two phase equilibria, and (2) the temperature coefficient of free energy.

SUMMARY

Calorimetric measurements of the heats of mixing of seven liquids with dihydromyrcene are used to estimate the heats of dilution of rubber by these liquids. Combining the results with free energies calculated from vapor pressure gives entropies of dilution which show significant deviations from the present statistical theory.

A thermodynamic study of rubber + methyl alcohol shows similar but larger deviations.

This work forms part of a program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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THE STRUCTURE OF POLYISOPRENES

IV. DOUBLE-BOND INTERACTION IN CERTAIN CARBALKOXY-SUBSTITUTED 1,5-DIENES *

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When unsaturated groups are components of a conjugated system it is well known that their individual properties are modified. Quantum mechanics now provides a sound theoretical basis for the extensive factual knowledge and even permits semiquantitative treatment of the simpler examples[1]. Much less understood and well defined are electronic interactions of more widely separated unsaturated centers and those in which formally saturated atoms or groups participate.

The latter type has featured prominently in the development of organic theory, and is identified with two modes of electronic polarization, viz., the inductive effect, having its origin in electrostatic forces, and the tautomeric effect, resulting from a tendency to covalency change. As data have accumulated, the complexity of electron response to environmental demand has become increasingly evident, and this is exemplified in the recognition of hyperconjugation. For some years the coexistence of the two effects acting oppositely has been assumed, e.g., the $-I + T$ character[2] of the halogens $\rightarrow$Cl, and a similar concept has recently been extended to the typically saturated alkyl groups[3]. Here, in addition to the commonly displayed inductive response, a tautomeric electron release is assigned to C—H bonds, and this conjugation of unsaturated centers with saturated bond electrons—hyperconjugation[4]—is thought to be of wide generality. Fundamentally, the reason for the presence of different polarizations in any one group remains enigmatical, although the respective operative conditions can often be well defined[5].

The related problem of double-bond interaction in nonconjugated dienes, which is the theme of this and the following paper, has evoked relatively negligible interest.

Müller[6] postulated neutralization of ethylenic activity across space to account for his observation, which Savard[7] claims to have confirmed, that geraniol is more transparent to ultraviolet light than the corresponding monoolefin, citronellol. This evidence must be accepted with reserve, however, in view of the well-known difficulty in obtaining pure homogeneous terpenes, and their susceptibility to oxidation. A similar condition has been envisaged in certain allylic ketones which show abnormal spectra[8] and in support is quoted loss of ketonic function on oxime formation—a doubtful criterion, since this reaction is known to be sensitive to less specific structural changes. The absence of correlation with more general theoretical principles obviates further

14

consideration of these ideas, but it is of interest to note the presumed diagnostic value of absorption spectra for mutual double bond saturation[9].

Much more significant is the work of Ingold and Shoppee, who generalized their conclusions in the theory of ring-chain mesomerism. The attention of these authors[10] was attracted by the pronounced change in physical and chemical properties in the series phorone, dibromophorone, bromohydroxyphorone (I, $X = Y = H$; $X = Y = Br$; $X = Br$, $Y = OH$, respectively). Color, refractivity, and parachor all decrease markedly, and chemical reactivity parallels the increasing saturation thus revealed. A comprehensive investiga-

tion indicated that, whereas bromohydroxyphorone is the saturated dicyclic compound (III), dibromophorone possesses hybrid character and cannot be formulated simply. The state was represented by (II), where two electrons from each double bond are shared over the dotted tracks and thereby effect a degree of bonding across space. In spite of consistent interrelationships, such as the correlation of the electronic nature of X and Y with the position of the derivative along the (I) → (III) scale, Ingold and Shoppee appreciated the limitations of conclusions derived from these highly tautomeric systems.

The problem was therefore pursued with a series of compounds first isolated by Guthzeit and Hartmann[11]. Reaction of sodium-dicarbethoxyglutaconic ester with iodine and similar condensations gave a crystalline solid whose analysis and preparation were consistent with the expected product (IV, $R = Et$). However, the compound was remarkably resistant to the usual olefinic reagents, and Guthzeit and Hartmann concluded that they had actually synthesized the bicyclobutane derivative (V). Support for this decision was obtained from

hydrolysis, halogenation, and alkylation experiments which indicated that two —$CH(CO_2Et)_2$ groups, each with replaceable hydrogen, were attached to the dicyclic nucleus. Furthermore, it was discovered that substitution at the extranuclear carbon atoms, as in (VI) and (VII), left the saturated character unimpaired, whereas products with nuclear hydrogen resulting from decarboxylat-

ing hydrolysis readily reduced permanganate—the inference being that such replacement afforded the means for disruptive nuclear attack.

In their reinvestigation, which included the corresponding methyl analogues, Ingold, Parekh, and Shoppee[12] confirmed that the octa-esters had all the reputed stability towards permanganate, but found equal resistance to halogenation and alkylation. Hydrolytic degradation proceeded in the stages described, but the decarboxylated derivatives all contained a combined molecule of water additional to the reported composition, and the alleged unsaturation of certain acids, e.g., that formulated as (VIII), proved to be fictitious. Because of these discrepancies and to explain ozonolyses, realized with difficulty, in which octa-esters underwent scission in agreement with formula (IV), the bicyclic formula (V) was rejected in favor of (IX) with resonance interaction of the double bonds, precisely as in dibromophorone[13]. The hexa-ester diacid (ex VI) was reformulated as (X, R = Et) with similar mesomerism, but the acids supposedly (VII) and (VIII) correspond to the cyclopentane derivatives (XI) and (XII). Slight, but significant differences appeared in the methyl series.
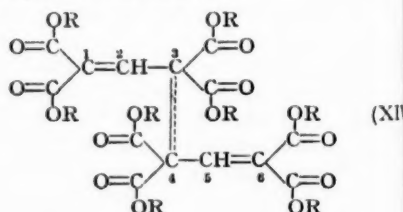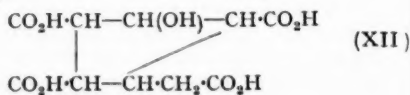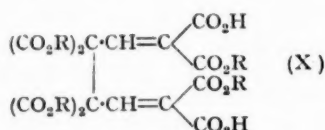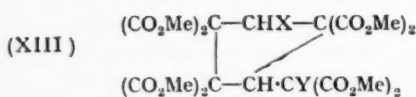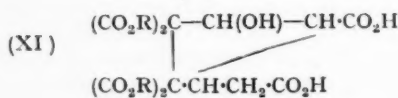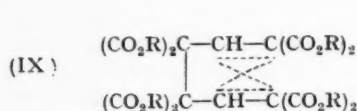
Dissolution of the octamethyl ester in cold dilute methyl-alcoholic sodium methoxide and subsequent acidification gave, not the hexa-ester diacid (X, R = Me) as in the ethyl series, but a compound of the ester and methyl alcohol (XIII, X = OMe, Y = H). This distilled without decomposition, in common with the other neutral esters containing combined water, e.g., esters of (XI) and (XII), but in contrast to the parent ester. Finally, electrolytic reduction gave a fully saturated dihydro-derivative, which also distilled unchanged and whose formulation as (XIII, X = Y = H) was further supported by relating its complete hydrolytic degradation product to the acid (XII).

The reactivity of the octa-esters is clearly paradoxical. On the one hand, the ethylenic bonds revealed by ozonolysis are highly resistant to the usual addenda; on the other, one molecule of a normally less active reagent combines easily under acid or alkaline conditions with concomitant cyclization. The double bonds appear to be interconnected in some way, and Ingold, Parekh, and Shoppee[12] identified this with the resonance electron exchange depicted in (IX).

The possibility of an alternative explanation was suggested by a complete x-ray structure analysis of the typical straight chain polyisoprene derivative, geranylamine hydrochloride[14], in which the central C—C bond of the 1,5-diene system formed by *trans*-linked isoprene units was found to be abnormally short. This feature is commonly associated with single bonds bounded by conjugated unsaturated centers, and although it is not entirely unexpected theoretically[15], yet the reason for its existence in a 1,5-diene remains obscure. A tentative explanation[14] in terms of hyperconjugation has yet to receive experimental support, and in simple systems this presents some difficulty.

Now the double bonds in the octa-esters are also 1,5-spaced, and it is reasonable to enquire whether their peculiar properties originate in similar but more extensive chain hyperconjugation. Superficial resemblances are at once apparent; cyclization following the addition of one molecule of reagent is common to the acid hydration and other reactions[16] of open-chain terpenes, and the relatively easy thermal breakdown at the central C—C bond[17] suggests facilitation by allylic resonance energy[18].

When the octa-ester is written as (XIV) the molecule is seen to possess high latent conjugation, whose development is a function of the electron-conducting capacity of the central C—C bond. Full conjugation creates a system of much lower energy, and the tendency to approach this state is a driving force offsetting the barriers imposed by single-bond insulation and by normal oribital hybridization, as is true indeed of any mesomeric system. Although the octa-esters differ from relevant hydrocarbons by the absence of hydrogen at carbon atoms 3 and 4 (XIV), yet Hughes and Ingold[5] and Hughes, Ingold, Masterman, and McNulty[19] have stressed that all quasi-unsaturated groups have hyperconjugative powers and this is certainly true of the highly polarizable carbalkoxyl groups. It may be noted that the carbon atoms forming the central bond are flanked by atoms contributing sp^2 bonding orbitals. Hence symmetrical sp^3 hybridization at the former may not be energetically favored, but instead a characteristic hybridization in which the hybrid bond has an added measure of electronic transmission over that of a normal single bond (possibly lower s/p ratio). In this sense, a normal double bond is simulated, but the absence of π electrons in the hybrid bond limits further similarity, *e.g.*, lack of additive function and ultraviolet absorption differences[20]. It is perhaps significant that the octa-esters are labile under conditions of electrical asymmetry where transmissive powers will be invoked to the full.

The consequence of chain hyperconjugation to molecular structure cannot be definitely predicted. In normal conjugation, a *trans*-planar configuration is usual, owing to enhancement of the resonance process, and a similar orientation about the hybrid bond, as in geranylamine hydrochloride, might well be anticipated in the octa-esters. Ring-chain mesomerism, on the other hand, necessarily requires a *cis*-arrangement. A discrimination between these theories becomes possible therefore by configuration analysis, and we have undertaken this by x-ray methods.

In general, intramolecular symmetry is not revealed by x-rays without recourse to a complete crystal structure analysis, but when it is used in symmetry operations effecting translations in the crystal lattice, systematic extinctions occur in the diffraction pattern that permit recognition from readily accessible data. A center of symmetry can be unequivocally identified providing that the compound crystallize in a particular lattice arrangement and that its molecular complexity be known from an independent source. In

practice, the latter condition can nearly always be met, and the success of the method essentially depends on Nature providing the former.

The octaethyl ester was examined first for symmetry character and proved to be an example from which no certain conclusion can be drawn. The crystals are triclinic with one molecule in the unit cell, and x-ray diffraction makes no distinction between the space group $P1$, with an asymmetric molecule, and $P\bar{1}$, with a centrosymmetric molecule. The absence of detectable pyroelectric effect indicates the latter, but does not provide the decisive evidence required.

The corresponding octamethyl ester, however, showed the presence of a center of symmetry unambiguously. The crystal system is monoclinic, and very careful indexing of oscillation photographs revealed the systematic extinction of the space-group $P2_1/a$. The combination of two-fold screw axis and glide plane requires four asymmetric structures per unit cell, but the observed density limits the number of molecules to two, and hence each molecule must provide two centrosymmetrically related units. A *cis*-configuration is impossible, and ring-chain mesomerism must be rejected as a structural feature of the crystalline state.

In addition to this approach, the unit cells of some derivatives and related compounds were measured in the hope that decisions between *cis-*, *trans-*, and cyclic structures might be made from a study of intermolecular packing. No systematic variations in molecular dimensions could be traced, and inspection of Stuart models makes it plain that the presence of several carbalkoxyl groups, each with some freedom of orientation, swamps the slight differences introduced by rearrangement of the central carbon framework. For example, the symmetrical *trans*-forms of the uncyclized esters fitted the unit cells excellently, but the *cis*- and dicyclic forms were not sufficiently different to make them inadmissible. At the same time, Ingold, Parekh, and Shoppee's experimental record[15], where repeated, was confirmed in all essential respects, both chemically and by x-ray molecular-weight determinations. We also identified three forms of the hexamethyl ester diacid (X, R = Me), one containing acetone of crystallization, and two forms of the acid esters (XI, R = Me and Et, respectively), one hydrated in each case. x-Ray data are given for crystalline methyl α,γ-dicarbomethoxyglutaconate, for its cyclobutane dimer (XVI,

(XV) $(CO_2Et)_2C-CH=C(CO_2Et)_2$ $(CO_2R)_2C——CH \cdot CH(CO_2R)_2$ (XVI)
                    | | |
                   Et $(CO_2R)_2CH \cdot CH—C(CO_2R)_2$
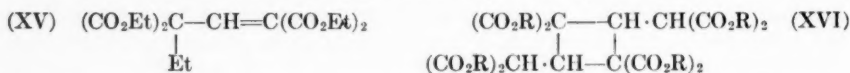
R = Me), which proved to be centrosymmetric, and for the two stereoisomeric dimers (XVI, R = Et) of ethyl α,γ-dicarbethoxyglutaconate. The configurations adduced for the latter on chemical grounds[21] are supported but not conclusively proved.

The nonexistence of ring-chain mesomerism in the crystal raises the question whether this is also true in the liquid phase where the anomalous reactivity is observed. Intramolecular association of the double bonds is considered to induce a state of lower energy, owing to the greater freedom of the electrons than when confined to normal bonds. If such a preferred state does exist in solution, a configurational change to the *trans*-structure on crystallization is possible only if accompanied by similar but intermolecular mesomerism and by improved crystal packing. We see no reason to expect special crystal forces and, in fact, the simple unit cells of the octa-esters, in contrast to the acid esters (XI, R = Me or Et), and particularly their hydrates, where hydrogen bonding is a structural condition, are indicative of nothing more than ordinary van der

Waals attractions. The direct examination of the molecular state in solution described in the accompanying paper supports this reasoning.

The x-ray data are only compatible with formula (V) if the carbon nucleus is assumed to be planar. This is highly improbable stereochemically, and the rejection of the bicyclo-structure on chemical and spectral evidence[22] is therefore confirmed.

There is then no alternative but to accept the open-chain formula and to seek another explanation of the unusual chemistry. Depression of double-bond activity may be due to the deactivating carbalkoxyl substituents or to steric hindrance. Ethyl α,γ-dicarbethoxy-α-ethylglutaconate (XV), where the double bond has the same group environment, is also resistant to additive reagents. Comparative experiments show that it reduces potassium permanganate in acetone solution roughly fifteen times as rapidly as the octaethyl ester at the same molar concentration. Although this rate difference, which is half the true comparative value if the double bond is the seat of oxidative attack and if the rate is directly proportional to olefin concentration, might be attributed to the heavier side-chain substitution in the octa-ester, present knowledge indicates that this interpretation is probably inadequate. Although other substituted glutaconic acids show normal, if greatly reduced, olefinic activity[23], yet Ingold, Parekh, and Shoppee[12] have isolated the hexa-ester diacid from the action of permanganate on the octamethyl ester, a result which recalls the inertness of the double bond and the lability of the alkyl group in tetraethylethane towards the same reagent[24]. Unless it can be shown, contrary to these indications of more profound reactivity difference, that the measured oxidation is initiated at the double bond in both cases, rate comparison has little value. Nevertheless, we think that the common substitutional influences must be reckoned with in assessing additive function in these systems.

Of greater significance is the cyclization propensity. This is characterized by simultaneous addition of a molecule A–B such that A adds to one olefinic center, B to the other—a feature clearly similar to 1,4-addition to butadiene except that valency redistribution occurs through internal bonding instead of by double-bond shift. As Ingold et al. argued, acceptance of partial double-bond interaction seems inevitable, and we suggest that this has now to be identified with chain hyperconjugation. In effect, this result generalizes a principle familiar in the aromatic series, e.g., the benzenoid character of pyrrole, furan, and thiophen and perhaps of cyclohexadiene[20], and the ionicity of the CH_2 group in the series cyclopentadiene, indene, fluorene, viz., that the intervention of a saturated group does not entirely thwart the development of full molecular conjugation.

EXPERIMENTAL

No original preparations were undertaken, but certain differences were found from the melting-point data of Ingold, Parekh, and Shoppee[12], whose values are therefore given in parentheses for comparison. The density units are g. per cc.

Methyl α,γ-dicarbomethoxyglutaconate.—M. p. 50–51° (43°)[25]. Large triclinic crystals tabular on (100), with cell dimensions $a = 12.26$, $b = 8.79$, $c = 8.30$ A., $\alpha = 115°$, $\beta = 115°$, $\gamma = 113°$; $V = 666$ A.[3]. Hence, with 2 molecules in the cell, the observed density of 1.38 gives M, 277 (Calc.: 274).

Octamethyl ester.—M. p. 141° (139°) (Found: C, 48.35; H, 4.85; M, by vapor-pressure equilibration of a benzene solution against olive oil, 540 ± 30; cryoscopically in benzene, 530 ± 30. Calc. for $C_{22}H_{26}O_{16}$: C, 48.35; H, 4.8%;

M, 546). Crystallizes from acetone and a little light petroleum (b. p. 60–80°) in monoclinic prisms with forms {010}, {001}, {110}. Cell dimensions: $a = 10.39$, $b = 14.60$, $c = 8.37$ A., $\beta = 103.5°$; $V = 1234$ A.^{3}. Very careful indexing of oscillation photographs revealed systematic extinctions of ($0k0$) absent for k odd, and ($h0l$) absent for h odd with no exceptions. The space-group is therefore $P2_1/a$, requiring 4 asymmetric structure units. The observed density is 1.48 and that calculated for 2 centrosymmetric molecules in the cell is 1.47.

Octaethyl ester.—M. p. 86° (Found: C, 54.7; H, 6.45. Calc. for $C_{30}H_{42}O_{16}$: C, 54.7; H, 6.45%). Triclinic crystals with {100}, {102}, {001}, {010}, commonly developed, also occasionally {011} and {101}. Cell dimensions: $a = 12.24$, $b = 8.72$, $c = 8.72$ A., $\alpha = 97.5°$, $\beta = 104.5°$, $\gamma = 107.5°$; $V = 855$ A.^{3}. Absence of pyroelectric effect indicates a space group $P\bar{1}$ with one centrosymmetric molecule. d(obs.) $= 1.275$, whence $M = 657$ (Calc.: 658).

Comparative reducing power of the octaethyl ester and ethyl α,γ-dicarbethoxy-α-ethylglutaconate towards permanganate.—Attempts to measure the reduction in acetone solution quantitatively by an absorptionmeter were abandoned, partly because of the development of a brownish tinge as the pink color faded, with subsequent coagulation of the manganese dioxide, and partly because the octaester invariably gave an opaque solution as reaction proceeded. Instead, a deficit of permanganate was used, and the time for complete disappearance of color measured. A trace of acid was added to eliminate adventitious variations due to possible sensitivity to pH conditions, *e.g.*, induction period. In the absence of thermostatic temperature control (2° range), the solutions were maintained under the same conditions throughout the reaction. A typical experiment was: Solution A: octa-ester, 0.0213M; KMnO$_4$, 0.00052M; HCl, 0.00003N. Solution B: ethylated tetra-ester (p. 214), 0.0215M; KMnO$_4$ and HCl as in A. Solution C: KMnO$_4$ and HCl as in A. A was decolorized in 52 hours, B in 4 hours, and C had faded slightly in 52 hours. Three similar experiments gave a mean reduction time ratio for A/B of 15 ± 4.

Hexamethyl Ester Diacid (X, R = Me).—Difficulty was experienced in obtaining suitable crystals for x-ray work, and crystallization behavior was capricious generally. Two apparently isomorphous and visually indistinguishable forms were isolated from acetone: an anhydrous form (1), and an unstable solvated form (2) which lost solvent on standing in air. The former was usually obtained, the latter rarely, and the conditions favoring the formation of either crystals were not discovered. Form (1) had m. p. 225–226° (decomp.) (218°) (Found: C, 46.3; H, 4.5. Calc. for $C_{20}H_{22}O_{16}$: C, 46.3; H, 4.3%); monoclinic plates with $a = 18.4$, $b = 8.55$, $c = 14.3$ A., $\beta = 92°$; $V = 2248$ A.^{3}. The space-group is $C2/c$ with 4 centrosymmetric molecules, or Cc with 8 asymmetric molecules; d(obs.) $= 1.55$, whence $M = 523$ (Calc.: 518). Form (2) had the same m. p. after loss of solvent; on standing, the crystals became opaque and this change was reflected in the analytical figures (Found: after *ca.* 7 days, C, 48.7; H, 5.15; after *ca.* 10 days, C, 48.3; H, 5.0; after 24 weeks, C, 46.25; H, 4.35; equiv., by titration, 263. $C_{20}H_{22}O_{16},2C_3H_6O$ requires C, 49.2; H, 5.35%; M, 634); cell dimensions: $a = 23.00$, $b = 8.05$, $c = 16.75$ A., $\beta = 93°$, $V = 3100$ A.^{3}. Space-group also $C2/c$ or Cc; d(obs.) $= 1.35$, whence $M = 629$. The acid was slightly soluble in hot water, the cooled solution depositing a third crystalline form (3) as very small triclinic prisms of the same m. p. (Found: C, 46.05; H, 4.4%); cell dimensions: $a = 10.01$, $b = 8.24$, $c = 8.20$ A., $\alpha = 118°$, $\beta = 109°$, $\gamma = 108°$; $V = 555$ A.^{3}; $n = 1$; d(obs.) $= 1.57$, whence $M = 524$.

Hexaethyl ester diacid (X, R = Et).—M. p. 191–193° (193°). Triclinic prisms, with $a = 11.07$, $b = 8.92$, $c = 8.55$ A.; $\alpha = 119°$, $\beta = 106°$, $\gamma = 94°$; $V = 715$ A.^{3}. d(obs.) = 1.385, whence $M = 596$ (Calc.; 620). Absence of pyroelectric effect indicates one centrosymmetric molecule in the cell.

Hexaethyl ester diacid chloride.—M. p. 66.5–67° (65–66°). Monoclinic prisms, with $a = 27.86$, $b = 8.73$, $c = 12.96$ A., $\beta = 98.5°$; $V = 3117$ A.^{3}; $n = 4$; d(obs.) = 1.355, whence $M = 635$ (Calc.: 639). Space group $P2/a$.

Dihydrooctamethyl ester (XIII, X = Y = H).—M. p. 156°, with previous softening (149°) (Found: C, 48.25; H, 5.2. Calc. for $C_{22}H_{28}O_{16}$: C, 48.2; H, 5.15%). Monoclinic prisms with $a = 19.63$, $b = 12.19$, $c = 11.51$ A., $\beta = 109°$, $V = 2603$ A.^{3}; $n = 4$; d(obs.) = 1.40, whence $M = 548$ (Calc.; 548). Space-group $C2/c$.

Methyl cyclopentane hydroxy-acid ester (XI, R = Me).—Anhydrous (1) and hydrated (2) forms were isolated on crystallization from water. Form (1) had m. p. 248–250°, with previous softening (245°) (Found: C, 45.8; H, 4.85. Calc. for $C_{16}H_{20}O_{13}$: C, 45.7; H, 4.8%). Orthorhombic bipyramids, with $a = 26.62$, $b = 18.65$, $c = 16.34$ A.; $V = 7616$ A.^{3}; $n = 16$; d(obs.) = 1.47, whence $M = 421$ (Calc.: 420). Form (2) afforded orthorhombic needles with $a = 62.7$, $b = 26.66$, $c = 12.15$ A.; $V = 20310$ A.^{3}; $n = 32 + 256H_2O$; d(obs.) = 1.47, whence $M = 562$ ($C_{16}H_{20}O_{13},8H_2O$ requires M, 564).

Ethyl cyclopentane hydroxy-acid ester (XI, R = Et).—Again, anhydrous (1) and hydrated (2) forms were isolated. The first, crystallized from ether and ligroin, had m. p. 153–154° (152°) (Found: C, 50.4; H, 5.95. Calc. for $C_{20}H_{28}O_{13}$: C, 50.4; H, 5.9%); orthorhombic pyramids, usually penetration twins, with $a = 29.46$, $b = 19.45$, $c = 16.47$ A.; $V = 9437$ A.^{3}; $n = 16$; d(obs.) = 1.345, whence $M = 478$ (Calc.: 476). The *hydrate* (2) crystallized from water (Found: C, 48.4, 48.4; H, 6.1, 6.15. $C_{20}H_{28}O_{13},H_2O$ requires C, 48.5; H, 6.1%) in monoclinic prisms with $a = 19.08$, $b = 15.61$, $c = 8.80$ A., $\beta = 112°$; $V = 2430$ A.^{3}; $n = 4$; d(obs.) = 1.32, whence $M = 483$ (Calc.: 494). Space-group $P2_1/a$. Guthzeit and Hartmann[11] reported a trihydrate, $C_{20}H_{26}O_{12},3H_2O$, *i.e.*, $C_{20}H_{28}O_{13},2H_2O$, but, in agreement with Ingold, Parekh, and Shoppee[12], we failed to isolate this. The monohydrate now described is new.

Dimer of methyl α,γ-dicarbomethoxyglutaconate (XVI, R = Me).—M. p. 222° (Found: C, 48.45; H, 5.25. $C_{22}H_{28}O_{16}$ requires C, 48.2; H, 5.15%); monoclinic prisms, with $a = 11.00$, $b = 14.18$, $c = 8.13$ A., $\beta = 99.5°$; $V = 1250$ A.^{3}; $n = 2$; d(obs.) = 1.44, whence $M = 542$ (Calc.: 548). Extinctions correspond to the space-group $P2_1/n$. The molecules must, therefore, possess a center of symmetry, and their configuration is probably analogous to that of the corresponding ethyl dimer, m. p. 103°, as proposed by Ingold, Perren, and Thorpe[21].

Dimers of ethyl α,γ-dicarbethoxyglutaconate (XVI, R = Et).—(1) M. p. 103° (Found: C, 54.4; H, 6.7. $C_{30}H_{44}O_{16}$ requires C, 54.5; H, 6.7%); tabular triclinic crystals, with $a = 11.81$, $b = 9.49$, $c = 9.37$ A., $\alpha = 111°$, $\beta = 111°$, $\gamma = 112.5°$; $V = 875$ A.^{3}; $n = 1$; d(obs.) = 1.25, whence $M = 658$ (Calc.: 660). Space-group probably $P\bar{1}$, with centrosymmetric molecule. (2) M. p. 86–87° (Found: C, 54.35; H, 6.8%); short monoclinic needles, with $a = 26.28$, $b = 12.49$, $c = 21.42$ A., $\beta = 101.5°$; $V = 6890$ A.^{3}; $n = 8$; d(obs.) = 1.27, whence $M = 660$. Space group $A2/a$.

SUMMARY

A peculiar lack of olefinic reactivity, combined with a facility for cyclization of methyl and ethyl $\Delta^{1,5}$-hexadiene-1,1,3,3,4,4,6,6-octacarboxylates, has

been attributed by Ingold, Parekh, and Shoppee to ring-chain mesomerism. A reinvestigation of these and related compounds has now been made by using x-ray methods, and it is shown that the crystal structure of the methyl ester is incompatible with the *cis*-configuration required for such interspatial double-bond saturation. A radical disruption of a mesomeric system by crystallization from solution is improbable and, an earlier formulation incorporating a bicyclobutane nucleus being rejected on chemical grounds, it is necessary to seek a new interpretation of the anomalous reactivity. We suggest that the determinative condition is hyperconjugation throughout the carbon framework of the molecule, and discuss this in relation to 1,5-dienes generally.

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THE STRUCTURE OF POLYISOPRENES

V. ULTRAVIOLET ABSORPTION SPECTRA OF CERTAIN CARBALKOXY-SUBSTITUTED 1,5-DIENES, AND THE CHARGE-RESONANCE SPECTRA OF GLUTACONIC ESTER ENOLATE IONS *

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It was pointed out in Part IV (preceding paper) that, both in empirical hypotheses and in the electronic theory of ring-chain mesomerism, double-bond interaction across space was thought to create a more saturated molecular condition which a short-wave shift in ultraviolet absorption would serve to reflect. Thus in the phorone series the normally unsaturated phorone is bright yellow dibromophorone in which ring-chain mesomerism is postulated as only faintly colored, and the saturated dicyclic bromohydroxyphorone as colorless[1]. Similar ring-chain mesomerism has been attributed to the octa-esters (I, R = Me or Et) to explain their peculiar chemical behavior[2] but x-ray examination now shows that the methyl ester and almost certainly the ethyl ester do not possess *cis*-configurations in the crystalline state. Interspatial

(I) $(CO_2R)_2C=CH—C(CO_2R)_2$

$(CO_2R)_2\overset{|}{C}—CH=C(CO_2R)_2$

$(CO_2R)_2C=CH—\overset{|}{\underset{X}{C}}(CO_2R)_2$ (II)
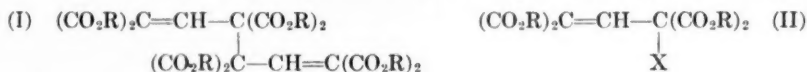
double-bond saturation is thus invalidated, but only by indirect arguments was it possible to extend the conclusion to conditions where the anomalous reactivity is actually observed. Spectrographic data were, therefore, required for two main reasons: (1) ring-chain mesomerism analogous to that envisaged in dibromophorone demands similar spectral consequences, and (2) the molecular state in solution is directly investigated. In addition, the purity of preparative intermediates could be checked, and it has been possible to confirm the basic structure assigned to certain derivatives.

The spectrographic approach is essentially a comparison of the octa-esters with a chemically normal analog (II). However, of intrinsic interest to tautomeric and spectral theory is the rather complex spectroscopic and chemical behavior of the α,γ-dicarbalkoxyglutaconic esters (II, X = H), and this is discussed separately in the second part of this paper.

Spectrographic examination of the octa-esters (I), some derivatives, and related compounds.—The ultraviolet absorption of the octaethyl ester (I, R = Et) had been examined qualitatively, by Hartmann[3] and adduced in support of the original bicyclobutane formulation[4], a conclusion definitely inacceptable in the light of the present work. Measurements in alcoholic solution of the octaethyl and octamethyl esters, together with those of ethyl α,γ-dicarbethoxy-α-ethyl

glutaconate (II, R = X = Et), are recorded in Figure 1, where ϵ is plotted per tetraester residue.　The absorption of all these compounds is very similar to that exhibited by the parent tetraester (II, R = Et, X = H) in hexane or

acidified alcohol, and is typical of the normal $C\overset{*}{=}C\!-\!CO_2R$ chromophore, *e.g.*, crotonic acid, $CH_3 \cdot CH : CH \cdot CO_2H$, has λ_{max}. 2040 A., $\epsilon = 12,000$ in alcohol[5]. The absorption processes at the double bonds in the octa- and tetraesters are evidently the same and, of special importance to the present problem, no absorption shift is apparent which is remotely comparable with that from phorone
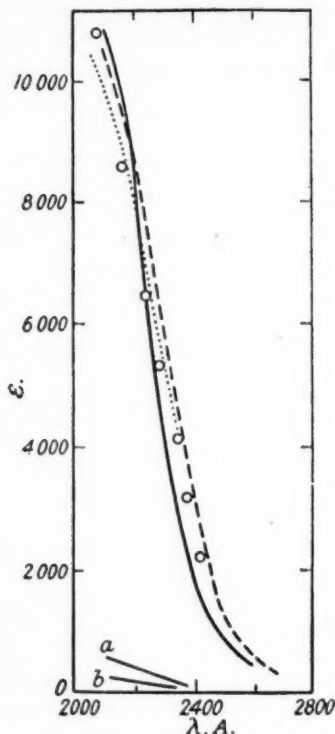
Fig. 1.—Spectra in ethyl-alcoholic solution.

—————————　Ethyl α,γ-dicarbethoxy-α-ethylglutaconate.
— — — —　Octaethyl ester.
．．．．．．．．．．　Octamethyl ester.
O O O　Hexamethyl ester diacid.
a　Ethyl cyclobutane octa-ester; dihydroöctamethyl ester; octamethyl ester—methyl alcohol compound.
b　Hydrolytic degradation product (tetramethyl ester diacid) (ϵ per half-molecule).

to dibromophorone.　Support is thus derived for the arguments presented in the preceding paper that the nonexistence of ring-chain mesomerism in the crystal applies equally to the dissolved state.　Moreover, the correctness of the bicyclobutane formula is rendered still less probable, since conjugation of carbalkoxyl groups with a saturated, if strained, carbon nucleus would certainly be characterized by a distinct and less absorptive spectrum, as is the comparable cyclopropane conjugation[6].

The evidence was surveyed in Part IV which led Ingold, Parekh, and

Shoppee to formulate the hexa-ester diacid derivatives as structural analogs of the octa-esters but, in contradiction to Guthzeit and Hartmann, to recognize a profound structural change on hydrolytic degradation. The absorption of the hexamethyl ester diacid can be compared in Figure 1 with that of the acid-ester degradation product, the dihydroöctamethyl ester, and the octamethyl ester–methyl alcohol compound, three substances which, according to Ingold, Parekh and Shoppee are related cyclopentane derivatives. The large spectral difference fully supports the proposed change in structural type and, indeed, comparison with the saturated cyclobutane dimer of ethyl dicarbethoxyglutaconate (Figure 1), and consideration of the actual intensity values leave no doubt that the structural change is from molecules with two double bonds, each conjugated with carbalkoxyl groups, to nonolefinic carbalkoxy-compounds.
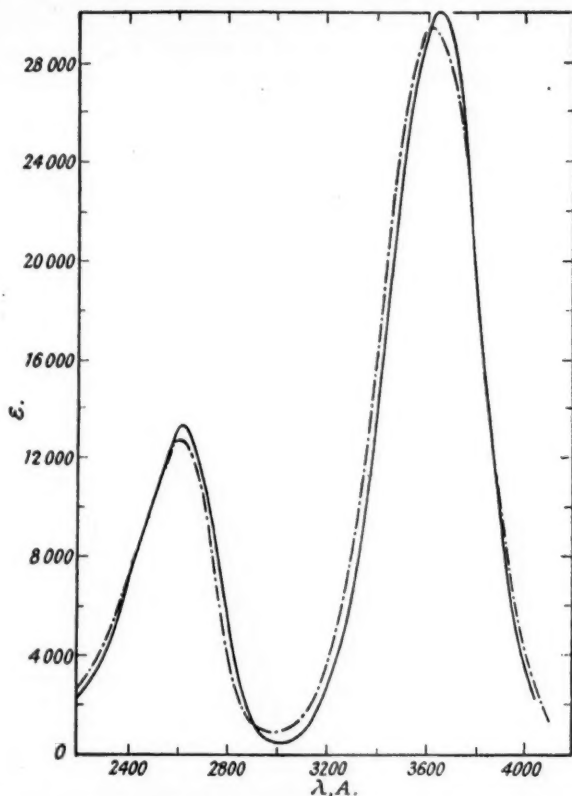
FIG. 2.—Sodio-derivatives of dicarbethoxyglutaconic esters in ethyl-alcoholic solution
——————— Ethyl ester   —.—.—.— Methyl ester

Normal substitutional influences seem inadequate to account for the chemical peculiarities of the octa-esters, and it has been suggested that the unique molecular condition is determined by chain hyperconjugation[7]. It has already been shown by Bateman and Koch[8] that the marked bond shortening in geranylamine hydrochloride, also attributed to chain hyperconjugation in 1,5-dienes, is not detectable by absorption in the quartz ultraviolet region. A

similar interpretation of the chemistry of the octa-esters is compatible therefore
with the spectral evidence, although its nonspecificity precludes its use in a
confirmatory sense.

Spectra and tautomerism of glutaconic acid derivatives.—Stobbe and Wildensee[9]
studied the automeric behavior in various solvents of ethyl α,γ-dicarbethoxy-
glutaconate (II, R = Et, X = H) spectrographically by the Hartley-Baly
method, and by rough colorimetry with ferric chloride. The enol form, fully
characterized by the sodio-derivative (X = Na), exhibited intense selective
absorption at approximately 2600 A. and especially at approximately 3600 A.,
and these bands also appeared, though much more feebly, when the parent
ester was dissolved in neutral ethyl alcohol. The alcoholic solution, however,
did not obey Beer's law and the increased absorption intensity observed on
dilution was recognized as a measure of increasing enol content. In ether,
chloroform, hexane, or acidified alcohol, only fairly strong end absorption oc-
curred, and if the α-carbon atom was ethylated (X = Et) similar but slightly
greater end absorption resulted in either neutral or acidified alcohol or in
hexane.

Our measurements on the pale yellow sodio-derivatives of the methyl and
ethyl tetraesters (II, X = Na, R = Me or Et) in ethyl-alcoholic solution are
shown in Figure 2. The corresponding green cupric derivatives have similar
spectra in the ultraviolet (Figure 3), but Beer's law is not obeyed. The absorp-
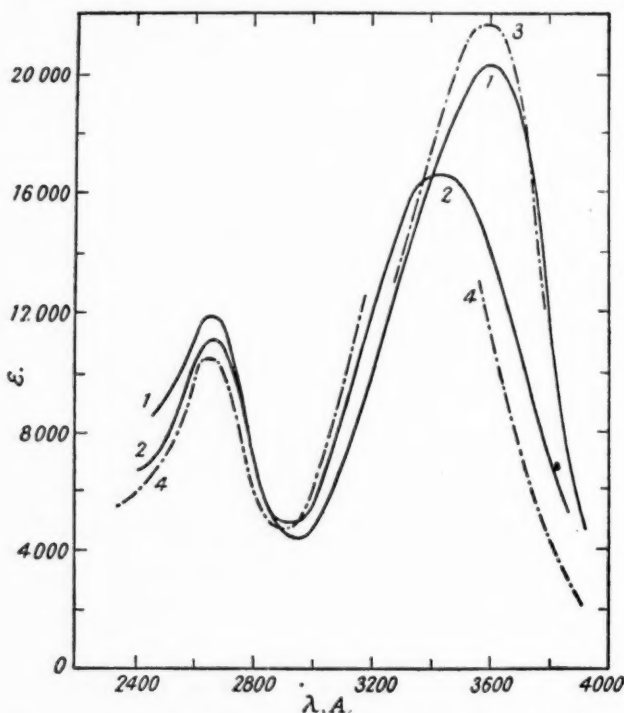
FIG. 3.—Copper salts of dicarbalkoxyglutaconic esters in ethyl-alcoholic solution

1. Ethyl ester, [Cu++] = 10^{-4} M
2. Ethyl ester, [Cu++] = 5.2×10^{-4} M
3. Methyl ester, [Cu++] = 3×10^{-3} M
4. Methyl ester, [Cu++] = 7.5×10^{-4} M

tion bands are displaced and less intense, but the curves suggest that at infinite dilution the spectra of the sodio-compounds will be exactly reproduced.

Neutral alcoholic solutions of the parent tetraesters show the long-wave band of the respective sodio-derivatives at precisely the same wave-lengths, and the other band, although obscured by end absorption at the higher concentrations, is indicated by the inflection in the curves obtained from the more dilute solutions (Figure 4). The intensity of these bands increases markedly on dilution, and if we assume that the pure enol form of the ester has the same absorption intensity as the sodio-compound, the equilibrium concentration of enol at the dilutions studied is readily calculated.

Ester	Concn. (M)	Intensity, ϵ	Enol (%)
Tetramethyl	0.0103	170 ($\lambda_{max.}$ = 3630 A)	0.6
Tetramethyl	0.0004	3250	11
Tetraethyl	0.0125	135 ($\lambda_{max.}$ = 3660 A)	0.4$_5$
Tetraethyl	0.0005	2350	8
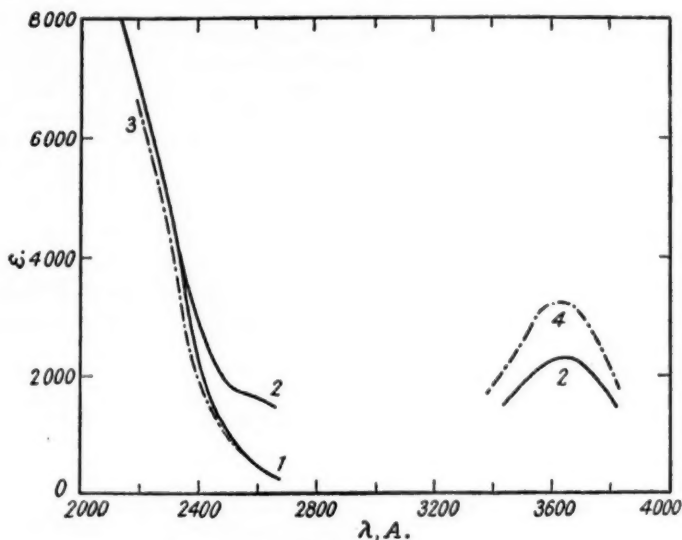
Fig. 4.—α,γ-Dicarbalkoxyglutaconic esters

1. Ethyl ester in cyclohexane
2. Ethyl ester in alcohol (5 × 10⁻⁴ M)
3. Methyl ester in 5% alcoholic H_2SO_4
4. Methyl ester in alcohol (4 × 10⁻⁴ M)

In acidified alcohol, selective absorption disappears entirely (Figure 4), and only end absorption corresponding to the $C=C—CO_2R$ chromophore is observed.

The classical enol formula (III, X = H) is inadequate to account for this

$$\begin{array}{c} RO \\ \diagdown \\ C=C—CH=C(CO_2R)_2 \\ \diagup \qquad | \\ XO \qquad CO_2R \\ (III) \end{array}$$
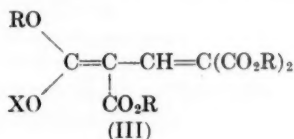
varied behavior, and the following points call for comment: (1) The free esters in neutral alcohol and their sodio-derivatives exhibit the same near ultraviolet absorption bands; (2) the main enol band occurs at remarkably long wave-lengths; (3) solutions of the copper derivatives show the enol bands displaced and of reduced intensity, but the full intensity at the usual wave-lengths is apparently developed at infinite dilution; (4) solvent effects on the keto-enol equilibrium.

(1) The first point implies that the hydrogen enol and its salt have the same electronic structure, in contrast to the enols of ketones such as ethyl aceto-acetate, acetylacetone, etc., whose ionic salts always absorb more or less differently (at longer wave-lengths) and where it has been inferred that the salts possess somewhat different types of bonding[10].

(2) The structural factors which govern the wave-length position of the first strong absorption band of conjugated compounds are now fairly well understood, mainly owing to the experimental work of Hausser and Kuhn on polyenes[11] and of Brooker on cyanine dyestuffs[12].

Hausser and Kuhn and their collaborators found that the position of maximum absorption shifts to longer wave-lengths as n increases in the series A—$[CH=CH]_n$—B. In practice, absorption spectra of natural and synthetic polyenes of this type have often been employed as structural criteria, since a reliable value of n can usually be deduced from λ_{max}. The degree of conjugation present in the enol formulation (III) is similar to that of sorbic or muconic acid,
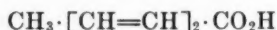
$$CH_3 \cdot [CH=CH]_2 \cdot CO_2H$$

and $CO_2H \cdot [CH=CH]_2 \cdot CO_2H$, which have λ_{max}. 2540 and 2630 A., respectively[13]. Absorption beyond 3600 A. is not in fact observed until the homolog $CH_3 \cdot [CH=CH]_5 \cdot CO_2H$ is reached[14], so it is obvious that a structural condition other than, or additional to, ordinary conjugation is operative in the enols of the tetraesters.

(IV) [structure: benzothiazole ring with S, C=CH—[CH=CH]$_n$—C bridge to benzothiazole with N; NEt substituent]

(V) [structure: benzothiazole with S, C—[CH=CH]$_n$—CH=C bridge; $\overset{+}{N}Et$]

(VI) [structure: benzothiazole, S, C=CH—[CH=CH]$_n$—C; NEt and $\overset{+}{N}Et$]

(VII) [structure: benzothiazole, S, C—[CH=CH]$_n$—CH=C; $\overset{+}{N}Et$ groups]
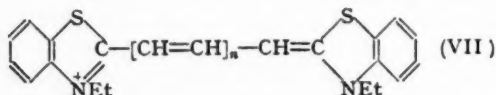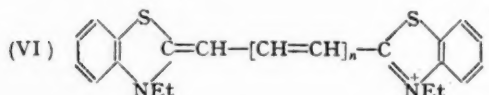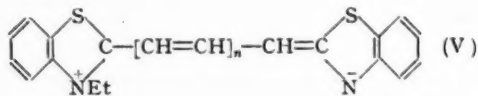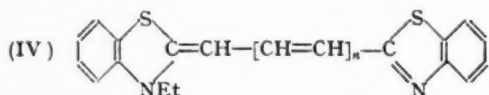
Brooker[12] has pointed out that for compounds formally conjugated to the same extent, deepening of color, as regards both λ and ϵ, is found in those structures which allow of effectively complete resonance degeneracy. The anhydro-base (IV), for example, is not fully mesomeric because the extreme

canonical structure (V) is at a higher energy level. The corresponding ethiodide (VI) (a cyanine dye), of equal formal conjugation, is completely valency degenerate because the extreme alternative structure (VII) is now strictly equivalent, and this dye absorbs at considerably longer wave-lengths and also much more intensely than its parent base.

The enol ions of α,γ-dicarbalkoxyglutaconic esters are clearly much simpler examples of the cyanine structural system, the two forms (VIII) and (IX) being energetically identical. All the ester groups will participate in the charge
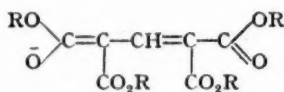
(VIII)   (IX)
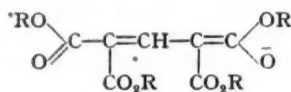
(X)
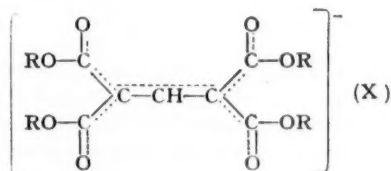
distribution, so the real state of the ion is as schematically shown in (X), in which six electrons are shared over the dotted tracks. This interpretation of the long wave-length absorption also throws light on the general behavior of glutaconic ester-type tautomerides which, in short, is determined by the high stability of the enol anion[15].

(3) The reduced absorption of solutions of the copper derivatives must be attributed to complex formation where coördination of the metal atom tends to localize the anionic charge in its neighborhood. Two of the four extreme canonical structures will thus be preferentially stabilized, a process known to result in short-wave spectral displacement[16]. The equilibrium may be written:
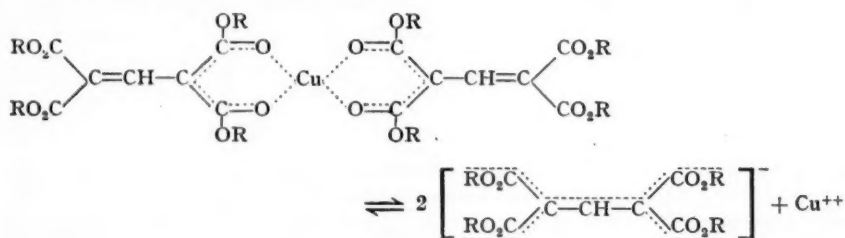
where reduced resonance in the chelated organic residue is compensated for by increased resonance in the metallic valencies.

(4) In ketones proper, enolization is promoted by nonionizing solvents and repressed by hydroxylic solvents, i.e., the reverse of the behavior shown by the tetraesters (II) which enolize exclusively in the latter media, and the equilibrium is not usually affected by dilution with the same solvent or by addition of acid[17]. Differences between these two tautomeric types, however, are not as fundamental as the solvent effects cursorily suggest.

The equilibrium in the glutaconic esters is represented by $AH \rightleftharpoons A^- + H^+$, where AH and A^-, the ketoform and enol ion, respectively, are the sole recognizable entities. There are no absorption bands corresponding to a third tautomer such as the undissociated enol. When A^- is sufficiently stabilized by resonance, enolization will be promoted by proton acceptors to an extent depending on their basic strength, and inhibited completely by stronger acids and by aprotic solvents. The equilibrium is merely that of a simple acid-base system, where the energy of ionization of the C—H bond is reduced by an amount approaching the resonance energy gained on enol-ion formation.

The position is less straightforward in ketones proper, since the hydrogen enol now has real existence. The equilibria are as shown in the inset, where KH, E—H, and E^- are the keto-form, enol, and enolate ion, respectively.
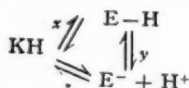
The enol is energetically stabilized either by intramolecular[18] or, less commonly, by intermolecular[19] hydrogen bonding. In consequence, the chelated enols, in common with other hydrogen-bonded structures such as salicylaldehyde and o-hydroxyacetophenone, absorb at longer wave-lengths than their O-alkylated derivatives[20]. Enol formation is favored by conditions of minimum polarity; hydroxylic solvents, either by acting as alternative electron donors or by effecting charge distribution, inhibit severely. In the glutaconic esters, a hydrogen bridge across the 7-membered resonating unit (see X) is highly improbable stereochemically, while bonding within either malonic end group would interfere with full molecular mesomerism. Hence, the conditions for hydrogen enol stability are absent, and in solvents such as hexane only the keto-structure exists.

Equilibrium (z) exactly simulates that described for the glutaconic esters. The absorption bands of the enol ions (E^-), exhibited by the sodium salts formed in water or alcohol[20] occur at longer wave-lengths and have much
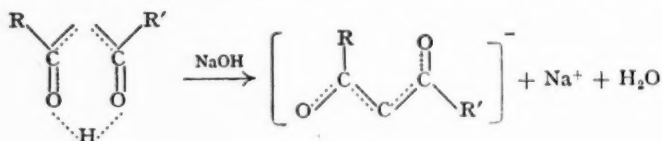
greater intensity than those of the chelated hydrogen enols. This is probably due to fuller mesomerism and to the setting up of a resonating charge[21]. The intensity increase may be further associated with the greater spatial elongation of the chromophore when the chelate ring is broken[22].

The position may be summarized thus: (1) In glutaconic esters, hydroxylic solvents and bases in general favor enol-ion formation; in aprotic solvents only the keto-form can exist. (2) In ketones proper and malonic ester where chelation is similarly possible, enol-ion formation is favored as in (1); aprotic solvents promote hydrogen enol formation.

Of further interest in the correlation of absorption spectra with structure in highly resonating systems is the spectrum of the so-called ethoxylactone (XI) obtained by loss of ethyl alcohol when attempts are made to distil ethyl α,γ-dicarbethoxyglutaconate (see Experimental Section). With bands at

2500 and 3550 A. of practically identical intensity (Figure 5), the spectrum in cyclohexane is not dissimilar to the reported spectra of other α-pyrones[23], although the intense near-ultraviolet absorption is again notable. Guthzeit and Dressel[24] found that the compound was decomposed by alcohol, but we have yet to obtain evidence that it exists at all in hydroxylic solvents. If

(XI)

(XII)
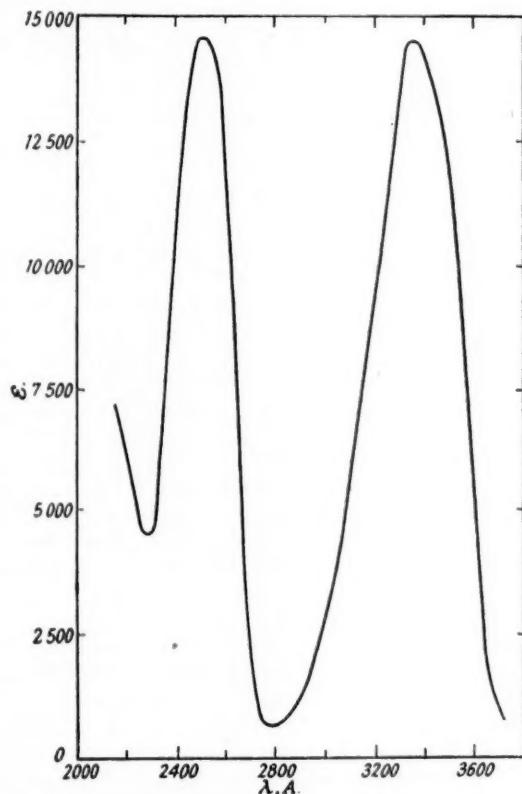
FIG. 5.—Lactone from ethyl dicarbethoxyglutaconate, in cyclohexane solution

dissolved in alcohol and immediately examined spectroscopically, only the original glutaconic ester can be detected, and this finds a parallel in the ferric chloride reaction which, entirely absent in cyclohexane, becomes identical with that of the glutaconic ester on the addition of a few drops of alcohol. We suggest tentatively that the compound may really be the internal salt (XII). This symmetrical structure is highly degenerate in the distribution of the negative charge, and it follows that hydroxylic solvents effect decomposition subsequent to internal ionic dissociation. Further pursuit of this topic awaits more extensive knowledge of the chemistry and spectroscopy of related lactones and their derivatives than it has yet been possible to obtain.

EXPERIMENTAL

The spectrographic technique was as detailed by Bateman and Koch[8]. Compounds not otherwise described were those employed for x-ray examination, and are analytically specified in Part IV.

Sodio-tetra-esters (II, X = Na).—(1) The ethyl ester, prepared according to Ingold and Perren[25] and recrystallized four times from aqueous alcohol, had m. p. 260*. (2) Guthzeit, Weiss, and Schaefer[26] were unable to crystallize the crude methyl ester obtained from condensation of methyl sodiomalonate with chloroform, but describe an extraction procedure for isolating the pure sodio-derivative, m. p. 247–248°. We were unable to obtain pure specimens in this way (Found: C, 43.25; H, 4.4; Na, 8.4. Calc. for $C_{11}H_{13}O_8Na$: C, 44.5; H, 4.4; Na, 7.75%), although m. p.'s as high as 258–259° were observed. The pure compound was prepared by shaking the pure parent ester (II, R = Me, X = H; 2 g.) in ether with sodium carbonate (0.38 g.) in water, evaporating the aqueous layer under reduced pressure, extracting the residue with acetone, isolating the extract, and repeating the extraction. This solution yielded a very pale yellow powder, m. p. 264° (Found: C, 44.75; H, 4.4; Na, 7.5%).

Copper salts of the tetra-esters (II, X = $\frac{1}{2}$Cu).—(1) That from the ethyl ester, recrystallized three times from ethyl alcohol, had m. p. 177°. (2) For the preparation of the *salt* from the methyl ester, an aqueous solution of the crude sodio-compound was treated with aqueous cupric sulfate, and the precipitate crystallized three times from ethyl alcohol, m. p. 246–248° [Found: C, 43.1; H, 4.35; Cu, 10.5. $(C_{11}H_{13}O_8)_2Cu$ requires C, 43.2; H, 4.3; Cu, 10.4%].

Dicarbalkoxyglutaconic esters (II, X = H).—(1) *Ethyl ester.*—Evaporation of the extract after decomposing the pure sodio-compound with dilute aqueous acid in the presence of ether gave a clear syrup (Found: C, 54.35; H, 6.75. Calc. for $C_{15}H_{22}O_8$: C, 54.5; H, 6.7%) whose spectrum was virtually identical with that of the pure crystalline methyl ester. As the usual distillation technique under reduced pressure causes decomposition with pyrone formation, short path, nonebullioscopic, distillation between surfaces at 90° and −78° at a pressure of 10^{-5} mm. of mercury was carried out. Even this distillate contained 3% of pyrone as estimated by the very sensitive spectroscopic method (Found: C, 54.55; H, 6.7%. Cf. analysis of the pyrone). (2) *Methyl ester.*— The recrystallized copper derivative, dissolved in chloroform, was shaken with dilute aqueous sulfuric acid until the organic layer became colorless. After being dried and evaporated under reduced pressure, the chloroform solution yielded a colorless syrup which eventually crystallized, m. p. 49°. Recrystallization from ether-ligroin gave the pure ester, m. p. 50–51° (Found: C, 48.25; H, 5.15. Calc. for $C_{11}H_{14}O_8$: C, 48.2; H, 5.15%). Ingold, Parekh, and Shoppee give m. p. 43°. Submitted to nonebullioscopic distillation (surface temperatures 80° and −78°), the distillate in this case was free from pyrone and was spectrally identical with the pure crystals.

Pyrone (XI or XII).—The solid obtained on distillation of the ethyl tetra-ester under 11 mm. was recrystallized successively from ether and cyclohexane and had m. p. 95° (Found: C, 54.9; H, 5.75. Calc. for $C_{11}H_{16}O_7$: C, 54.8; H, 5.6%).

Ethyl α,γ-dicarbethoxy-α-ethylglutaconate.—Prepared by Thole and Thorpe's method[27], this had b. p. 214°/25 mm. (Found: C, 57.0; H, 7.4. Calc. for $C_{17}H_{26}O_8$: C, 57.0; H, 7.3%). Selective absorption was entirely absent in cyclohexane as well as in alcoholic solution. A fractionated specimen, b. p. 120–121°/0.05 mm., prepared according to Guthzeit and Dressel[28], gave incor-

rect analyses (Found: C, 57.8, 58.0; H, 7.5, 7.6%) and reduced permanganate in acetone 10–15 times as rapidly as the pure compound, but its absorption was only slightly greater. The nature of the impurity was not ascertained.

This and the preceding paper form part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

SUMMARY

Spectral evidence supports the conclusion reached in Part IV that ring-chain mesomerism in methyl and ethyl $\Delta^{1,5}$-hexadiene-1,1,3,3,4,4,6,6-octacarboxylates is nonexistent in solution, just as in the crystalline state. The data are not inconsistent with chain hyperconjugation in these molecules. The marked change in structural type that follows the addition of one molecule of hydrogen or hydrolytic reagent has been verified spectrographically.

The spectra of methyl and ethyl α,γ-dicarboxyglutaconic esters and their sodium and cupric derivatives have been measured in various solvents, and their tautomeric behavior compared with that of other keto-enols. Of special interest is the intense long-wave absorption band of the enolate ions, which are recognized as simple structural analogs of the cyanine dyes giving rise to similar charge-resonance spectra. A preliminary comment is made on the present accepted structure of ethyl 6-ethoxy-α-pyrone-3:5-dicarboxylate.

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REACTIVITY OF ISOPRENIC AND ANALOGOUS HYDROCARBONS TOWARDS THIOCYANIC ACID AND DITHIOCYANOGEN *

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By analogy with hydrogen halides and hydrogen sulfide[1] it is reasonable to expect thiocyanic acid to react with olefins, and it has been reported by Kharasch, May, and Mayo that it will add to isobutylene at room temperature to give a mixture of tert.-butyl thiocyanate and isothiocyanate. Under similar conditions in the present work, the only product that was obtained from cyclohexene and thiocyanic acid was a small quantity of an amorphous powder, probably mainly a perthiocyanic acid, formed by elimination of hydrogen cyanide from three molecules of thiocyanic acid. This tendency towards decomposition of the reagent prevented the use of elevated temperatures, and when methyl thiocyanate (a potential source of SCN and Me radicals by thermal decomposition) was heated at 170° with 1-methylcyclohexene and a little benzoyl peroxide (as catalyst), it underwent but slight reaction, the drop or two of product giving analytical values which suggested that it might be an impure adduct. Attempts to catalyze the addition of thiocyanic acid to rubber included the use of ultraviolet irradiation, and of aluminum chloride or ferric chloride as catalyst. The most successful of these attempts was with ultraviolet light, but even then the product contained only 1.95% of sulfur, which represented 6% addition to the double bonds of rubber.

Although dithiocyanogen is known to add readily to many unsaturated compounds[2] the only reference to its reaction with cyclohexene indicated that addition was very slow, and no product was isolated[3]. It has now been established that 1-methylcyclohexene reacts very readily with nascent dithiocyanogen in chloroform. With rubber the reaction proceeds readily with preprepared dithiocyanogen, as has been observed by several workers, and by varying the quantities used products were prepared in which 7–100% of the unsaturation was destroyed. In every case gelling started after about 1 hour, increased concurrently with addition of dithiocyanogen, and was not complete for several hours. With nascent dithiocyanogen, however, reaction was complete within a few minutes.

Addition of thiocyanic acid to rubber.—A 10% ethereal solution of thiocyanic acid was prepared from sodium thiocyanate by the method of Klason[4]. Treatment of a 10% carbon tetrachloride solution of milled crepe with this solution in daylight at 15° gave products containing, after 24 hours 0.07% of sulfur, and after 120 hours 0.245%. A similar experiment in cyclohexane solution at 0° in the dark gave values of 0.32% and 0.25% respectively.

When a mixture of a 10% carbon tetrachloride solution of milled crepe (50 ml.) and 10% ethereal thiocyanic acid (100 ml.) contained in a quartz

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flask was irradiated with ultraviolet light for $1\frac{1}{4}$ hours, only 0.05% of sulfur entered the rubber. The experiment was repeated, acetone being added as a photosensitizer and the mixture sealed under nitrogen (at 360 mm.) in a Pyrex tube. After 16 hours' irradiation at 25–30° the product contained 1.95% of sulfur.

With ferric chloride and aluminum chloride as catalyst after 3 days in daylight at 15° products were obtained containing 0.6% and 0.85% of sulfur, respectively.

Addition of dithiocyanogen to 1-*methylcyclohexene.*—Lead thiocyanate (40 g.) was stirred as a suspension in chloroform (120 ml.) and methylcyclohexene (10 g.) at 0°, and phenyl iodochloride (29 g.) added in small quantities. The mixture was stirred at 0° for 5 hours and then kept overnight at that temperature. The lead chloride was filtered off, and excess of dithiocyanogen destroyed by shaking the solution with sodium thiosulfate solution (40 g. in 120 cc. of water). From the dried solution, chloroform was removed by distillation at atmospheric pressure, and iodobenzene and unchanged methylcyclohexene similarly at 13 mm. pressure. 1 : 2-*Dithiocyano-*1-*methylcyclohexane* distilled at 100–106°/0.1 mm. as a heavy, viscous, yellow oil, which solidified on cooling to 0° (Found: C, 50.8; H, 5.9; N, 12.9; S, 30.4. $C_9H_{12}N_2S_2$ requires C, 50.9; H, 5.7; N, 13.2; S, 30.2%).

Addition of Dithiocyanogen to Rubber.—Dithiocyanogen was prepared by reaction of lead thiocyanate (8 g.) with bromine (3.2 g.) in carbon tetrachloride or disulfide (100 cc.) at 0°. To 25 ml. of this solution were added 100 ml. of a 1% carbon disulfide solution of milled acetone-extracted crepe. After 40 minutes some of the product was separated by precipitation with alcohol (Found: S, 1.6%), and the remainder, which started gelling after about $1\frac{1}{2}$ hours, was separated by washing with alcohol at the end of 20 hours (Found: S, 14.85%). The time of initiation of gelling was not changed by the substitution of carbon tetrachloride as solvent; with 10% rubber solutions in either solvent, gelling commenced after 30 minutes.

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THE STUDY OF THE MECHANISM OF POLYMERIZA-
TION REACTIONS BY MEANS OF
SIZE-DISTRIBUTION CURVES *

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In this paper we shall consider polymerization reactions where the mean life of the active chain centers is very small compared with the half-life of the total reaction. The polymerization under certain conditions of acetylene, styrene, vinyl acetate and several other vinyl compounds is believed to be of this type.

The experimental investigation of the distribution curves of the products resulting from such reactions may be complicated by a number of factors. For example, as polymerization of pure liquid monomer proceeds the viscosity normally rises, which often renders it difficult to control the temperature. Moreover, the increase in viscosity implies that the long polymer radicals are relatively fixed in position while the monomer radicals may still diffuse readily; as a result the ratio of the velocity of termination to propagation of a radical may change throughout the reaction. Further, the rate of initiation of active radicals is, in general, a function of the changing monomer concentration. In addition, many polymerization catalysts, *e.g.*, benzoyl peroxide, decompose during the course of the reaction, thus modifying the speed of chain initiation. During later stages of the reaction there is an increased probability over the early period that "dead" polymer may become reinvolved in the reaction, and thus give rise to a certain amount of branching and cross-linking.

Adding to the difficulty of the interpretation of the curves are the complications of the mathematical treatment. Should the degree of polymerization be large, then the shape of the molecular yield chain length curve may be very different from that when the conversion is small, as is shown in Figure 1. To interpret the curves for large conversion the dependence of initiation rate on the catalyst and monomer concentrations must be known, and even then the resulting expressions may be far from simple. In all mathematical considerations of polymerization reactions, a ratio k_{t_r}/k_{p_r} constantly appears, where k_{t_r} is the velocity constant for termination and k_{p_r} that for propagation. In the development of a kinetic treatment some function has to be chosen for this ratio, and it is general to assume that it is a constant independent of chain length; an assumption which has to be carried over into distribution considerations if the conversion is large. The use of distribution curves when the conversion is small may, however, make possible the determination of the true form of this function.

A great simplification in the theoretical treatment, together with the avoidance of many of the practical difficulties, results if the reaction is only allowed to proceed to a small extent (5–10 per cent); preferably in dilute solution.

In the discussion which follows we shall assume that we are dealing with results obtained for a small conversion.

Distribution curves may be discussed conveniently in terms of the mechanism leading to the deactivation of the growing radical.
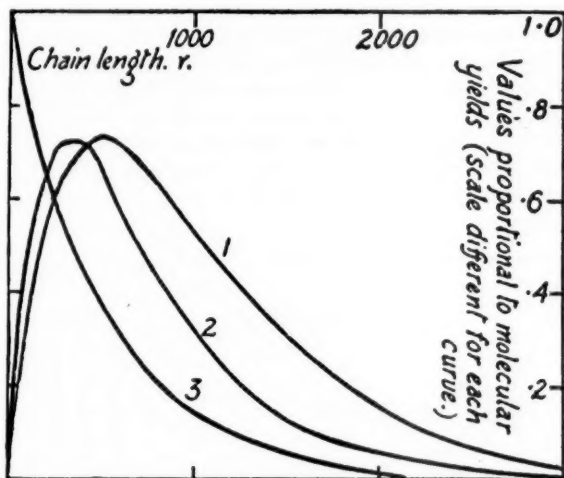
FIG. 1.—Relative chain distribution during the reaction. Initial number average chain length = 1000. Termination by combination.
Curve 1. Instantaneous.
Curve 2. 50 per cent conversion.
Curve 3. Total conversion.

If the final inert polymer molecule M_{r+1} results by termination by monomer M of the active radical P_r by collision:

$$P_r + M \rightarrow M_{r+1} \tag{1}$$

or if the polymer results by disproportionation where two radicals collide and separate:

$$P_r + P_s \rightarrow M_r + M_s \tag{2}$$

or, again, if a transfer mechanism is operative where a radical P_r collides with monomer and produces a new radical P_1, itself being rendered inert:

$$P_r + M \rightarrow M_r + P_1 \tag{3}$$

then in all these cases the final polymer molecule M_r has at some period been of lengths 1, 2 $\cdots$ r monomer units long.

The conditions for the formation of polymer M_{r+s} by combination are very different because, while this may result from the radicals P_r and P_s as follows:

$$P_r + P_s \rightarrow M_{r+s} \tag{4}$$

yet it may have been produced by the union of radicals P_{r+x} and P_{s-x}:

$$P_{r+x} + P_{s-x} \rightarrow M_{r+s} \tag{5}$$

We see, therefore, that the constituents of the final molecule M_{r+s} need never have been of lengths P_r or P_s.

These differences have a profound effect on the form of the size distribution curve (see Figure 2). In general, the first three mechanisms yield curves where the molecular yield (proportional to number of molecules of length r) falls continuously with increasing chain length, but the curve for the combination case shows a maximum.

The reason for the appearance of a maximum in the combination curve is not difficult to understand, for, as the chain length increases, the number of ways in which the final molecule may result also increases, but the number of long radicals is less than that of short ones. These two opposing effects produce the maximum. Under the simplest conditions, where $k_{t_r}/k_{p_r} = $ a constant, the maximum occurs at a chain length equal to half the number average. The more complicated case where this ratio is not constant has been discussed elsewhere[1], and as the expressions are difficult to manipulate we shall not discuss them further.
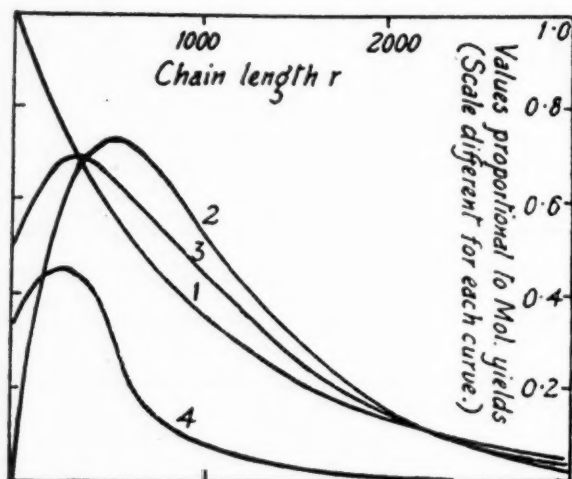
FIG. 2.—Instantaneous chain distribution.
Curve 1. Monomer, disproportionation, transfer.
Curve 2. Mutual combination.
Curve 3. Combination + transfer.
Curve 4. Monomer, disproportionation or transfer with k_{t_r}/k_{p_r} increasing $[k_{t_r}/k_{p_r} \alpha (1 + 0.004r)]$.

The other three cases (monomer, disproportionation and transfer) permit of the determination of the ratio k_{t_r}/k_{p_r} for different chain lengths and should thus be capable of checking the constancy of this ratio for various r values; a constancy which has so often been assumed in the kinetic treatment.

Consider the distribution curve, Figure 3, in which all molecules of chain length $r_1 + 1$, $r_1 + 2$ up to $r = \infty$ have at some stage passed through chain length r_1. In disproportionation and transfer the product M_{r_1} results from radicals P_{r1} and in the case of monomer termination from $P_{r_{1-1}}$, but for large values of r_1 this difference is negligible. Hence, for all three modes of termination we have:

$$\frac{\text{Velocity of termination of radical } P_{r_1}}{\text{Velocity of continuance of radical } P_{r_1} \text{ to give } M_{r+1} \cdots M_{\alpha}}$$
$$= \frac{\text{Ordinate at } r_1}{\text{Sum of ordinates from } r_1 + 1 \text{ to } r = \infty}$$

The denominator on the right-hand side is proportional to the shaded area under the curve; inserting this, and calling the resulting function β, we have:

$$\beta = \frac{\text{Ordinate at } r_1}{\text{Shaded area under curve}}$$

Provided the monomer concentration and the rate of initiation of chains is nearly constant over the period under consideration, then β is directly proportional to the velocity constant of termination divided by that of continuance.
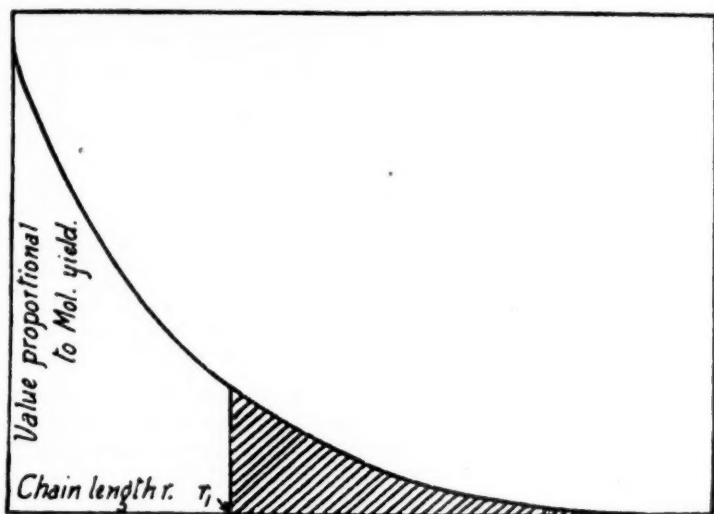
FIG. 3.—Graphical representation of derivation of β function, $\beta = \frac{\text{ordinate at } r_1}{\text{shaded area}}$

The β function can be used for all polymerization reactions where the product results by successive addition of monomer units.   Unfortunately there do not appear to be any published values for small conversions which might be examined by this method.

Strictly, the transfer reaction does not destroy an active center, for when the growing radical is deactivated by this process, a new center of growth is started. Transfer usually occurs in conjunction with one of the other terminating mechanisms.   If the deactivating reaction without transfer would give a curve resembling 1 in Figure 2, then the resulting curve with transfer is of the same type.   If combination and transfer occur together, the curve results from the supposition of curves 1 and 2 (Figure 2); the final curve resembling curve 1 if transfer predominates, and exhibiting a maximum if combination is the main factor.   Curve 3, Figure 2, is a curve of mixed type; it should be noted that it cuts the axis $r = 1$ at a finite value, and thus differs from pure combination.

A slight complication arises because, if the ratio k_{t_r}/k_{p_r} increases sufficiently rapidly as the chain length of the radical increases, then the curves resulting from termination by monomer, disproportionation or transfer may show a maximum and resemble the mixed transfer-combination curve.   Curve 4, Figure 2, is such a curve, where the ratio varies linearly with r, and has in-

creased fivefold from $r = 0$ to 1000. The reason for this behavior is under-standable when we realize that for these methods of termination the amount of active radical P_{r+1} is always less than that of P_r, but if P_{r+1} terminates more readily than P_r, then the resulting quantity of M_{r+1} may exceed M_r.

We can thus distinguish three types of curve.

Curve. Type.	Mechanism of Termination.
(1) The molecular yield decreases con-tinuously as the chain length increases. Figure 2, curve 1.	Either (1) (a) Monomer. $\quad P_r + M \rightarrow M_{r+1}$ or (b) Disproportionation. $\quad P_r + P_s \rightarrow M_r + M_s$ or (c) Transfer in conjunction with (a) or (b) above. $\quad P_r + M \rightarrow P_1 + M_r$
(2) Curve rises from zero at very small chain length, passes through maximum and then decreases as chain length in-creases. Figure 2, curve 2.	(2) (a) Combination $\quad P_r + P_s \rightarrow M_{r+s}$
(3) Curve commences at real finite values, passes through maximum, and decreases. Figure 2, curves 3 and 4.	(3) Either (a) Monomer, disproportionation or transfer, where velocity of ter-mination/propagation increases with chain length; or (b) Transfer and combination occur-ring at same time.

Many of the curves in the literature are useless for obtaining information on the reaction mechanism because the degrees of polymerization are not given. Only one curve (11 per cent polymerization of styrene[2]) appears to be available for small conversions; this is almost an ideal combination curve (Type 2 in above Table).

Finally, it should be stressed that, with complicated reactions involving several steps such as these polymerizations, the complete mechanism can only be solved by the study of many variables. As an example, monomer and disproportionation terminations can be distinguished kinetically, but dispro-portionation and combination cannot be separated by this means; while distribu-tion curves will clearly differentiate between disproportionation and combina-tion, but cannot be used to identify monomer termination as opposed to disproportionation.

SUMMARY

Some of the experimental complications which may attend the study of size-distribution curves are indicated. To obtain information on the mecha-nism from distribution curves, the degree of polymerization must be known. Most information can be obtained if the fraction polymerized is small (say up to 10 per cent polymerized) and if the rate of initiation is kept constant during this reaction period. Fortunately, those conditions which are best suited for the mathematical treatment of the process are also those which avoid many of the experimental complications.

Three main types of distribution curves may be distinguished; these are discussed in terms of the mechanism terminating the life of an active growing radical. Such distribution curves, taken in conjunction with other considera-tions, can greatly extend our knowledge of polymerization reactions.

ACKNOWLEDGMENT

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STRENGTH OF AMORPHOUS AND OF CRYSTALLIZING RUBBERLIKE POLYMERS *

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The strengths of unloaded vulcanizates and the action of active fillers differ greatly according to the types of elastomers from which they are derived.

These differences are not connected directly with the chemical compositions of the elastomers. Thus, for example, vulcanizates of natural rubber and synthetic isoprene rubber differ in strength in the ratio 10–15 to 1, whereas vulcanizates of Butyl rubber and of polychloroprene are very similar to natural rubber vulcanizates with respect to tensile strength.

These differences in tensile strength cannot be ascribed directly to differences in structure of the chains, linear or branched; linear polymers of styrene and of methyl methacrylate "vulcanized" by small admixtures of butadiene-benzene or dimethacrylate-ethyleneglycol have, in the elastic state, tensile strengths which are just as low as those of unloaded vulcanizates of sodium-butadiene rubber or of isoprene rubber.

The differences in tensile strength must, accordingly, be looked for in the different macroscopic properties of these polymers.

TABLE 1

Kind of rubber	Tensile strength of unloaded vulcanizate (kg. per sq. cm.)	Tensile strength of loaded vulcanizate (kg. per sq. cm.)	Tensile reënforcing effect of the active fillers
Rubbers of the first group			
Butadiene-rubber from sodium polymerization	15–25	120–180	from 5 to 12 times
Butadiene rubber	15–25	100–150	from 4 to 10 times
Buna-S	20–30	150–200	from 5 to 10 times
Buna-N	20–40	150–200	from 4 to 10 times
Isoprene rubber from sodium polymerization	15–20	100–150	from 5 to 10 times
Methyl rubber	20	80–120	from 4 to 6 times
Rubbers of the second group			
Natural rubber	200–300	300–325	from 1 to 1.6 times
Chloroprene rubber	150–200	200–250	from 1 to 1.7 times
Butyl rubber	250–350	300–350	from 1 to 1.4 times

Note.—In the table the highest authentic values of the tensile strength are given, which sometimes have been obtained on mixtures deprived of technical importance. The loaded vulcanizates contain the proportion of the filler which gave the highest tensile strengths.

In Table 1 the strengths of unloaded and loaded vulcanizates of different elastomers are compared. It is evident that all the rubbers can be divided into two sharply different groups, the tensile strengths of unloaded vulcanizates of the first group being of the order of 25 kg. per sq. cm. and those of unloaded vulcanizates of the second group of the order of 250 kg. per sq. cm.

The tensile strength of a vulcanizate of the first group is increased by the addition of filler up to the values characteristic of the vulcanizates of the second group, while the tensile strengths of the latter remain practically unaltered by loading.

Rupture of rubbers of the first and second groups takes place at extensions of the same order of magnitude, viz., 600–800 per cent. If the strengths of the vulcanizates of the first and second groups are compared under such conditions that the rupture takes place at small extensions, that is, by wearing away, fatigue or tearing, the vulcanizates of the two groups are found to behave in a quite similar way.

The high strengths of unloaded vulcanizates of the second group are always associated with high deformation. This seems to indicate that rubbers of the second group are strengthened by certain macroscopic changes which take place in the process of deformation.

Comparing the vulcanizates of the first and second groups from this point of view, we see that all the elastomers of the second group and the vulcanizates obtained from them crystallize, whereas vulcanizates of the first group do not crystallize. In the vulcanizates of the second group, partial crystallization takes place with extension. The small crystals play, according to our opinion, the role of an active filler, and increase the tensile strengths of the vulcanizates.

The unloaded vulcanizates of the second group thus behave in the case of large deformations as "self-loading".

The influence of the crystallization of vulcanized rubber on the shape of the stress-strain curve $F(L)$ was noted long ago by various investigators[1].

In 1940 Field,[2] in his studies of the crystallization of natural rubbers vulcanized by various methods, noted the parallelism between the increase in the amount of the crystalline phase and the strength, but did not ascribe the increase in the strength to the influence of the crystals as particles of an active filler.

The particles of crystalline rubber in the vulcanizate are very finely dispersed and very intimately connected with the amorphous phase. The mechanical properties of these crystals are apparently similar to the mechanical properties of paraffin crystals, *i.e.*, their true strength is very small. One cannot, therefore, tell *a priori* whether such crystals can actually cause a strengthening of the substance.

To solve this question, the following model experiments were carried out by us. The unloaded vulcanizate of sodium-butadiene rubber was swollen in fused paraffin or stearic acid. The breaking strengths of the swollen specimens were then measured at a temperature of 2–3° above that of the fusion point of the paraffin or stearic acid.

In this case, as can be seen from Table 2, the strengths were very low.

If, however, an extended specimen was cooled 2–3° below the fusion tem-

TABLE 2

TENSILE STRENGTH OF RUBBER FROM SODIUM-BUTADIENE RUBBER

Initial rubber (g.)	Swollen above the fusion temperature of the added component (g.)	Swollen below the fusion temperature of the added component (g.)	Weight (percentage) of the added component (with respect to the rubber) and kind of the substance
710	—	—	—
	200	2240	80 stearic acid
	320	1320	85 paraffin
	330	1840	65 palmitic acid

Note.—The tensile strength refers to the specimen. All the initial specimens had the same cross-section, and were torn away directly or after swelling. Each figure of the table represents an average of the values of 5 specimens.

perature of the paraffin or stearic acid, then, at the moment of crystallization, the hardness of the vulcanizate sharply increased, the curve $F(L)$ rose sharply, and rupture took place at a stress greater by a factor 4–11 than in the case of a liquid component, introduced in the process of swelling.

Furthermore the tensile strength of the rubber containing the crystalline phase exceeded by a factor 2–3 the tensile strength of the original vulcanizate. This model experiment confirmed the possibility of increasing the tensile strength of a vulcanizate at the cost of the crystallizing elastomer.

Let us consider in the light of this concept a few other properties of "self-loading" vulcanizates.

1. *Small influence of active fillers on the tensile strength of vulcanizates of the second group.*—This small influence is due to the fact that, near the breaking point, owing to the "self-loading", the vulcanizate contains a number of active fillers—crystals—lying close to the optimum one. Therefore the introduction of an additional active filler can change the strength in one or the other direction, although insignificantly.

2. *Sharp drop in the tensile strength of vulcanizates of the second group in a narrow temperature range.*—Figure 1 shows the dependence of the tensile
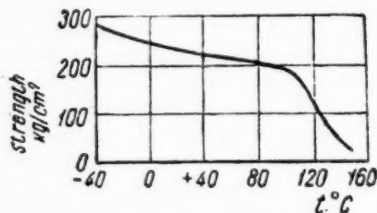
FIG. 1.—Dependence of the tensile strength of a vulcanizate of natural rubber on the temperature (according to Van Rossem[2])

strength of natural vulcanized rubber on the temperature. At a temperature about 120° the tensile strength decreases sharply from 260 to 20 kg. per sq. cm. in the case of an extension till the breaking point of the same order as before, about 800 per cent, is reached.

Comparing this curve with fusion temperatures of crystals at different extensions determined by von Susich[4] (Figure 2), we see that, in the case of elongations of about 800 per cent, fusion of the crystalline phase takes place at temperatures of 100–110° C.

Owing to the fusion of the crystalline phase, the strength of the rubber
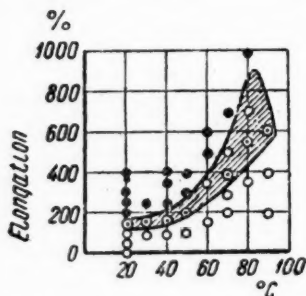
FIG. 2.—Melting temperature of crystalline rubber for various extensions (according to von Susich[4]) Points, crystalline; small circles, amorphous. Shaded region and circles with points, partially fused rubber.

drops from the curve of the "strength of the loaded rubber" to the curve of the "strength of unloaded rubber", as shown in Figure 1.

3. *A sharp optimum vulcanization of unloaded natural rubber* (determined by tensile strength).—Vulcanization decreases the tendency of rubber to crystallize. With increase in the number of space bridges, formed by sulfur or by some other vulcanizing factor, the critical extension at which the process of self-loading by the crystalline phase starts, is increased, while the quantity of the crystalline phase at the breaking point is decreased, which leads to a decrease of the strength. As soon as the critical extension becomes larger than that corresponding to the breaking point, the strength of the rubber sharply decreases, *i.e.*, it drops to the curve of the "strength of unloaded rubber".

4. *Large decrease in the work of rupture in the case of rapid deformations.*— The decrease in the work of rupture in the case of rapid deformations, which, according to our measurements, is especially strong in chloroprene rubbers, is connected with the fact that the velocity of crystallization becomes comparable with the rate of destruction, and the specimens are, therefore, destroyed at smaller contents of the crystalline phase than in the case of slow rupture.

The mechanism of the reënforcing action of active fillers in rubberlike substances consists mainly in the fact that the filler furthers the equalization of the stresses in the specimen.

In an elastic polymer the space macromolecular lattice is built up irregularly when it is strained; in some of its elements considerable overstresses arise which start the process of rupture, while the major part of the polymeric lattice is either not stressed at all or is stressed but slightly.

In a substance containing active fillers, a considerable part of the space lattice is adsorbed on the surface of the particles of the filler, and the corresponding binding is larger than the interaction force of the polymer molecules with each other and smaller than their strength.

Owing to such an intermediate value of the adsorption forces, the magnitude of the overstresses arising in a strained polymeric lattice cannot exceed the adsorption forces. As soon as the overstress in some region reaches this magnitude, the desorption of stressed chain begins, so that its stress does not increase with further deformation. Slightly stressed and nonstressed chains remain sorbed, and the stress on them rises.

The total stress of a strained specimen is thus distributed in a much more homogeneous way between the elements of its space lattice, and this leads to an increase in the modulus and the tensile stress. Rupture takes place when the possibility of an equalization of the stresses owing to desorption is exhausted.

The crystals play the same role, but the surface sorption is replaced in this case by packing of the polymer chains into a crystal.

As follows from the foregoing discussion, the high tensile strengths of certain unloaded rubbers are attributable to the "self-loading" by their crystalline phase in the case of extension.

This tensile strength has, therefore, nothing to do with the stability of the rubber against destruction by other kinds of deformation.

It is possible, therefore, that for the characteristics of the properties of rubbers in articles which suffer but slight deformations, it is quite needless to aim for high tensile strengths at large deformations.

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THE INFRARED SPECTRA OF COMPOUNDS OF HIGH MOLECULAR WEIGHT *

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Many methods are being used at present to explore the reasons for the differences in physical behavior of various types of polymers, plastics, rubbers and other compounds of high molecular weight. The peculiar rheological and electrical properties of many of these substances must be connected with the internal molecular structure and with the way in which the molecules can pack together in the solid and liquid states. Valuable information has already been obtained using the diffraction of x-rays, and some chemical methods have also given useful indications of the nature of the polymerization processes. The determination of molecular weights and chain lengths of fiberlike polymers has also led to important correlations. No method, however, has provided all the information which might enable us to formulate rules correlating properties with structure.

It is clear that any method which can examine the sample without the use of chemical reagents is of advantage, and from this standpoint spectroscopy should be useful. The infrared absorption spectra of substances of this type consist essentially of bands which correspond to the absorption of characteristic vibration frequencies of the whole molecule, or of particular units within it. Since, theoretically, no two molecules having a different nuclear skeleton have the same set of vibrational frequencies, we may expect small differences between the spectra of closely related molecules, and a careful analysis of the vibrational spectra may reveal the occurrence of special groups, or the arrangement of the nuclear skeleton within these molecules. For this analysis reference data from the spectra of simple related molecules may first be required. Apart from giving such fundamental structural information, however, the infrared spectra can be used empirically for many practical purposes. Small differences in the properties of samples of the same polymer can sometimes be correlated empirically with small differences in their spectra. The effect of different plasticizing or vulcanizing agents, leading for instance to cross-linking, can also be explored by spectral changes. On the fundamental side too, it is valuable from the standpoint of molecular dynamics to assemble data on long-chain polymeric substances as a basis for the calculation of the vibration frequencies of these molecules as systems of weighted chains. If the molecular dynamics could be understood more completely, it might prove a useful adjunct to the consideration of thermodynamic properties.

We have recently surveyed the infrared spectra of many compounds of high molecular weight belonging to different classes, partly to develop the experimental methods for examining these substances, but also to discover the type of information which can be obtained, and the most profitable lines for a more systematic attack. Papers describing some of the work are at present in the

press[1], and other detailed accounts will shortly be published. This article summarizes typical measurements and results on a variety of compounds, and is intended to illustrate the broad principles of the spectroscopic approach[2].

Most compounds of this type are usually examined in the solid state. Some can be obtained as thin films by rolling or cutting; these are measured as such. To bring out all the features of the spectrum several thicknesses of a given substance are desirable. The optimum thickness for different types of substance varies considerably. With essentially nonpolar materials it may vary from 0.1 mm. to several mm., but with other substances it may be necessary to have films thinner than 0.005 mm. Coherent films of many substances can be conveniently made by the evaporation of solutions from the surface of water or mercury, or from a heated glass plate, although in some cases it is difficult to remove the solvent completely. With other compounds it may be more satisfactory, and it is sometimes essential, to evaporate solutions on a hot rock salt or bromide plate, leaving an irregular solid layer; this method is suitable for the study of very thin layers of incoherent materials. Liquids are measured in a cell of the conventional type, and molten solids using a cell of the kind described in a previous paper[3]. Some solid powders have been studied by spreading them between rock salt plates moistened with carbon tetrachloride or a high-boiling paraffin.

One important group of compounds is the class of hydrocarbon-type polymers, parts of the spectra of some of which are shown in Figure 1. For some time it was thought that the polymerization of ethylene to form "polythene" gave a product having an uninterrupted straight chain of methylene groups. The infrared bands of polythene in the region of 3μ, where frequencies corresponding to the stretching vibrations of C—H linkages are absorbed, led Fox and Martin[4] to suggest that some methyl groups must be present. Polythene has relatively few absorption bands between $3-20\mu$. Reference to the spectra of paraffinic hydrocarbons enables us to identify most of the vibrations. Thus the band at 1460 cm.$^{-1}$ is connected with deformational motions of the methylene (CH_2) groups, and that at 725 cm.$^{-1}$ with a vibration of the long carbon-carbon chain. The band at 1375 cm.$^{-1}$ lies at the position characteristic of the symmetrical deformation of a methyl group, and this provides independent confirmation of Fox and Martin's earlier conclusion. By careful measurement of the optical densities and calibration of this methyl group band in branched chain paraffins, an estimate of the content of methyl groups can be made, and is found to be roughly one methyl group per fifty methylene groups. The feebler bands in the spectrum of polythene are less easily explained. One interesting feature however is the weak absorption at about 1720 cm.$^{-1}$, indicating $>CO$ groups. These could arise if oxygen were taken up during the catalytic polymerization; their presence at intervals along the carbon-carbon chain may markedly affect the electrical properties of the substance. On the other hand it is possible using ether or xylene to extract from polythene samples of lower molecular weight which may be rich in the ketonic material, and there is obviously scope for further work on this.

Polyisobutene also has a simple spectrum. The band at about 1485 cm.$^{-1}$ is connected with the deformational vibration of methylene groups, but it lies at a rather higher frequency than is usually found with paraffins (1460 cm.$^{-1}$). The symmetrical deformation of the methyl groups appears to be double (1370–1400 cm.$^{-1}$), and there is no obvious explanation for this, although it seems to occur with many paraffins having a pair of methyl radicals

attached to the same carbon atom. The bands of polyisobutene near 1200 cm.$^{-1}$ and 950 cm.$^{-1}$ are almost certainly due to vibrations of the distorted

carbon tetrahedron $--C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-$ present in the chain, and while exact calcu-

lations cannot yet be made, comparison with values for the vibration frequencies of such systems of C—C links suggests that there may be a slight weakening of the bonds in polyisobutene. The packing of methyl groups is known to be difficult in this case, and might well lead to strain and weakening of the carbon-carbon bonds.

The spectrum of a sample of Buna-85 made by the sodium-catalyzed polymerization of 1,3-butadiene is also shown in Figure 1. This polymerization
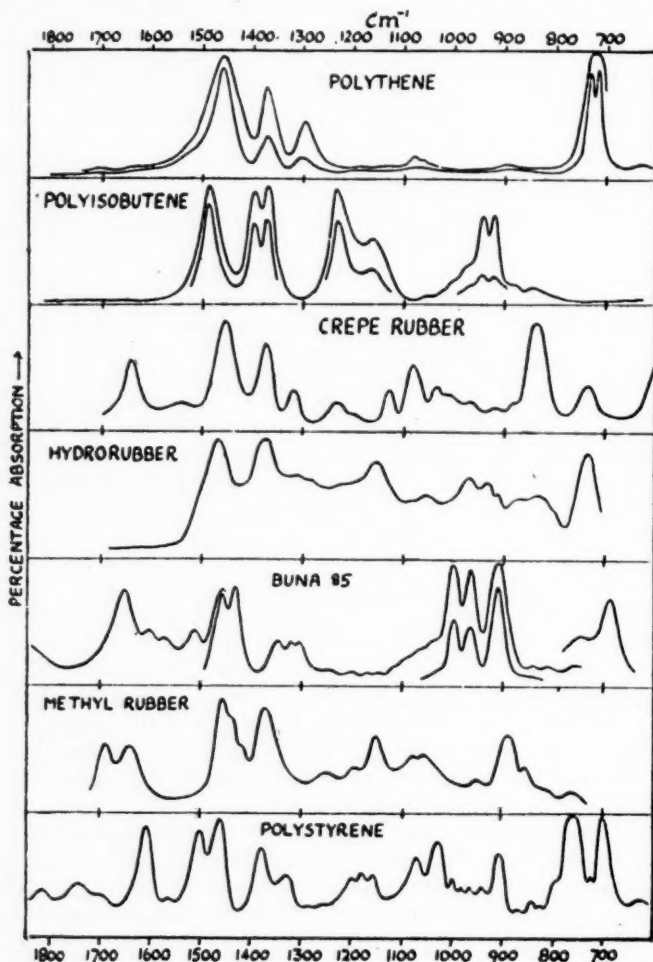
Fig. 1

can proceed by either 1,4-addition giving:

$$-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-$$

or by 1-2-addition, giving:

$$-CH_2-CH-CH_2-CH-$$
$$\quad\quad\quad | \quad\quad\quad\quad |$$
$$\quad\quad\quad CH \quad\quad\quad CH$$
$$\quad\quad\quad || \quad\quad\quad\quad ||$$
$$\quad\quad\quad CH_2 \quad\quad\quad CH_2$$
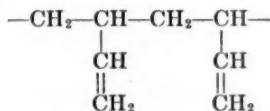
or by a combination of these processes. There are important structural differences in the two types of condensate. Thus, the former contains a recurring skeleton of the type $R_1CH=CH \cdot R_2$ and the latter of the type $R \cdot CH=CH_2$. From measurements on the infrared spectra of some simple olefins[1], we recently found a rule for differentiating between compounds of the type:

(1) $R \cdot CH=CH_2$ (2) $R_1CH=CHR_2$ (3) $R_1R_2C=CH_2$

in which R is an alkyl radical. Compounds of class (1) have two intense bands at about 909 and 990 cm.[-1]; those of class (2) have a strong band at about 965 cm.[-1], and those of class (3) a similar band at about 890 cm.[-1]. Compounds of the type $R_1R_2C=CHR_3$ were found to have a band at about 840 cm.[-1], though few compounds of this type have been examined. These characteristic frequencies are associated with deformational modes of C—H bonds attached to the C=C bond. The correlations were used originally in connection with the spectra of cracked polythenes, where the appearance of compounds of the isobutylene class (3) provide further evidence for the occurrence of side chain alkyl groups. Since this work was done, Rasmussen and Brattain have reached similar conclusions from measurements on a much larger series of olefinic hydrocarbons[5].

The spectrum of Buna-85 shows intense bands at 909, 965 and 990 cm.[-1] indicating that both 1,2- and 1,4-addition has occurred, and estimates can be made of the relative extent of each type. There is also the characteristic vibration frequency of the C=C bond at about 1650 cm.[-1]. The pair of bands at 1435 and 1460 cm.[-1] is probably connected with two slightly differing CH_2 deformations, such as might occur from the types $—CH_2—$ and $=CH_2$. The pendent vinyl groups revealed by bands at 909, 990 cm.[-1] may be expected to disappear if subsequent treatment leads to the formation of cross linkages.

Crepe rubber, which consists essentially of a recurring skeleton:

$$CH_3$$
$$\quad\quad |$$
$$-CH_2-C=CH-CH_2-$$
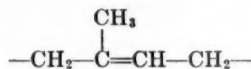
shows the infrared bands to be expected. Thus, there is that due to the C=C oscillation at 1645 cm.[-1], the CH_2 deformational mode at 1460 cm.[-1] and the CH_3 deformation at 1375 cm.[-1]. The band at 840 cm.[-1] corresponds to a trialkyl olefin, as explained above. Crepe rubber also has a band near 600 cm.[-1], and this spectral region is of interest with treated or vulcanized rubbers. In hydrorubber the C=C oscillation has disappeared, and the band at 735 cm.[-1] is similar to those found with some simple paraffins with a methyl group attached along the chain.

Two samples of methyl rubber have been examined, made respectively by the slow polymerization of 2,3-dimethylbutadiene in sunlight and by sodium. The curve of Figure 1 relates to the former, although no definite difference could be established between the two products. Here again, polymerization

could proceed by 1,4-addition, giving:

$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}=\underset{}{\overset{CH_3}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}=\underset{}{\overset{CH_3}{C}}-CH_2-$$

or by 1,2-addition giving:

$$-CH_2-\underset{\underset{CH_2}{\overset{||}{C}\cdot CH_3}}{\overset{CH_3}{\underset{|}{C}}}-$$
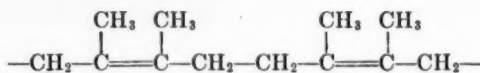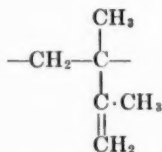
or by a combination of both. The infrared spectrum suggests the occurrence of both types of condensation. Thus the band at 890 cm.$^{-1}$ indicates that the isobutylene structure results from 1,2-addition, and as with Buna-85 the composite nature of the absorption at 1440–1460 suggests that two kinds of CH$_2$ deformation occur, presumably from the —CH$_2$— and =CH$_2$ groups. There is no characteristic band of the tetraalkyl olefin type, $R_1R_2C=CR_3R_4$, but the pair of bands at 1645, 1690 cm.$^{-1}$ would agree with the presence of two types of C=C link. Compounds of the type $R_1R_2C=CH_2$ would have absorption at about 1645 cm.$^{-1}$, and although no infrared data are available for comparison, the Raman frequencies of alkyl olefins[6] suggest that with tri- or tetraalkyl derivatives the C=C bond frequency lies higher at 1680–1690 cm.$^{-1}$. The methyl group deformation again appears intense at 1375 cm.$^{-1}$.

Many of the bands in the spectrum of polystyrene are common to simple aromatic hydrocarbons with one alkyl side chain. The intense absorption at about 760 cm.$^{-1}$ is similar to that found with isopropylbenzene. Substantially, the spectrum would agree with a simple head to tail condensation giving:

$$-\underset{C_6H_5}{\overset{}{\underset{|}{C}H}}-CH_2-\underset{C_6H_5}{\overset{}{\underset{|}{C}H}}-CH_2-$$
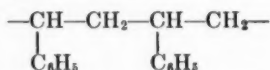
Insufficient data are yet available to decide whether some head to head condensation occurs, giving:

$$-CH_2-\underset{C_6H_5}{\overset{}{\underset{|}{C}H}}-\underset{C_6H_5}{\overset{}{\underset{|}{C}H}}-CH_2-$$
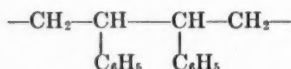
Polystyrene has a band at 1380 cm.$^{-1}$, however, which might indicate the presence of methyl groups, formed by inclusion in the chain of the grouping
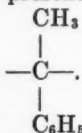
$$-\underset{C_6H_5}{\overset{CH_3}{\underset{|}{C}}}-.$$ This cannot, however, be regarded as proved, since the band in question may be due to a combination or overtone frequency.

In Figure 2 the spectra of several monomers related to the above polymers are shown. The important practical result is that the spectrum of a polymer always shows marked differences from that of its monomer, and this often provides an easy means for following the rate of a polymerization process, or for the determination of small amounts of residual monomer in the polymer.

Another immediate problem is whether the lengthening of a long chain polymeric system produces changes in the spectrum from which an estimate of

the chain length can be made. This does not seem very promising. Samples of polyisobutene having mean molecular weights between 1000 and 100,000 showed no significant change in the spectrum. Indeed the spectra of lower normal paraffins suggest that when there are more than about ten carbon atoms in the chain the spectral differences are very slight. Some differences found in the spectra of polythenes with molecular weights 1000–13,000 appear to have
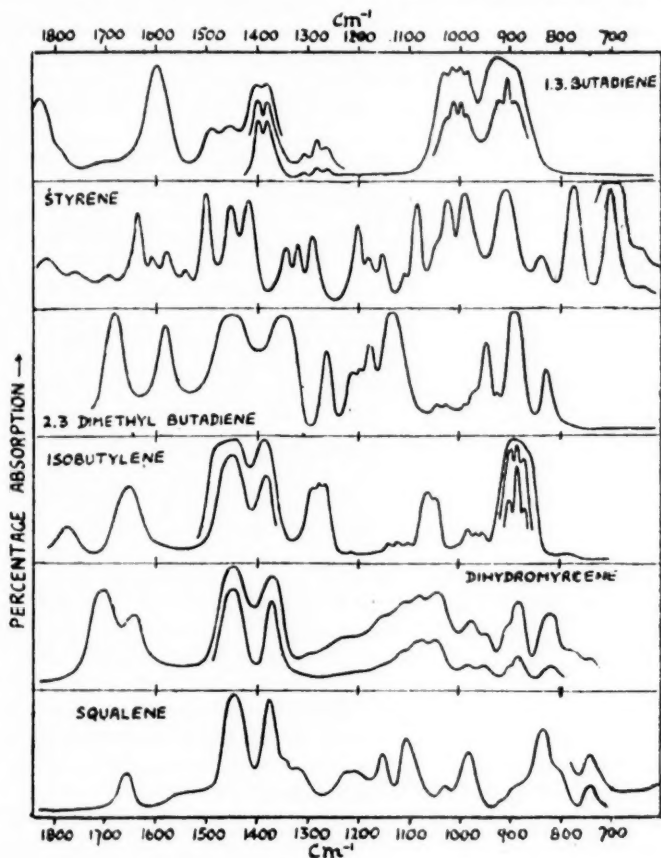
Fig. 2

arisen from the presence of varying amounts of substances other than the polythene chain itself. Figure 2 includes the spectra of samples of squalene (I) and dihydromyrcene (II), which seemed interesting in this connection as being closely analogous to a 6-unit and 2-unit rubber, respectively.

(I)

$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2-\left(CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2\right)_2-\left(CH_2-CH=\overset{\overset{\textstyle CH_3}{|}}{C}-CH_2\right)_2$$

$$-CH_2-CH=\overset{\overset{\textstyle CH_3}{|}}{C}-CH_3$$

(II)

$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH\cdot CH_3$$
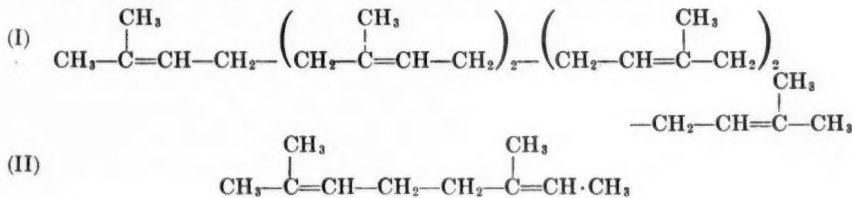
There are some marked similarities between the spectrum of squalene and that of crepe rubber, but several important differences. The band with squalene at 982 cm.$^{-1}$ is not easily explained and, until the purity of the squalene can be established, a more detailed consideration is unjustified; it may be noted, however, that some trimethylethylenes[7] have a band at about 980 cm.$^{-1}$, and this may therefore arise from the end groups in squalene.

There is no doubt that the sample of dihydromyrcene examined had become oxidized, as revealed by the band at about 1720 cm.$^{-1}$, and the broad background absorption in the region of 1100 cm.$^{-1}$. This latter region of absorption has been found with oxidized polythenes and oxidized rubbers, and will be considered later in connection with the spectra of esters, ketones, aldehydes, and other oxygenated compounds.

The method described above for determining the proportions of 1,2- or 1,4-addition in the polymerization of butadiene or alkyl butadienes can be applied to other processes to determine the mechanism of interpolymerization. Thus, when butadiene is condensed with acrylonitrile, straight chains might be formed of the type:

$$-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CN}{|}}{CH}-$$
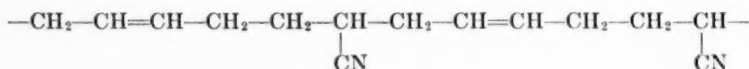
which will have the intense band at 965 cm.$^{-1}$, or pendant vinyl groups may remain, as in the structure:

$$-CH_2-\underset{\underset{\underset{CH_2}{\|}}{CH}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-$$
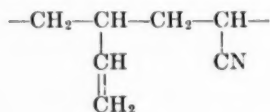
giving rise to the bands at 909, 990 cm.$^{-1}$. In a previous paper[8] we have described a sample of Perbunan in which the bulk of the condensation had proceeded by 1,4-addition, but in other samples of butadiene-acrylonitrile interpolymer variations seem to occur. Exactly similar considerations can be applied to Buna-S, the interpolymer between butadiene and styrene. If the factors which cause any particular type of addition to be preferred can be ascertained in this way, an important advance will be made in our understanding of the polymerization reactions. No general rules about this are so far apparent. Samples of butadiene polymerized under different conditions and with very different chain lengths appear to show a roughly constant ratio of 1,2- to 1,4-addition. On the other hand this ratio varies appreciably among the different chemical interpolymers. The chemical nature of the polymerizing components should have some effect on this ratio, and it seems unlikely that it can be determined by purely statistical considerations.

Another immediate problem is the determination of head-to-head or head-to-tail addition in the polymerization of vinyl compounds. Thus, the compound $CH_2=CH-X$ may lead to

$$-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}- \quad \text{or} \quad -CH_2-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH}-CH_2-$$
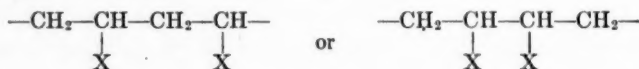
It seemed possible that a comparison of the spectra of the polymers with those of other compounds, such as $X \cdot CH_2CH_2CH_2X$ or XCH_2CH_2X would throw light on this. Figure 3a shows the spectra of polyvinyl acetate, polymethyl

acrylate and polymethyl methacrylate with those of the corresponding mono-
mers. The absorption of these polymers is far more intense than that of the
nonpolar hydrocarbon-type substances, and the spectra are more complex.
In analyzing the spectra a first step was to decide which bands are primarily
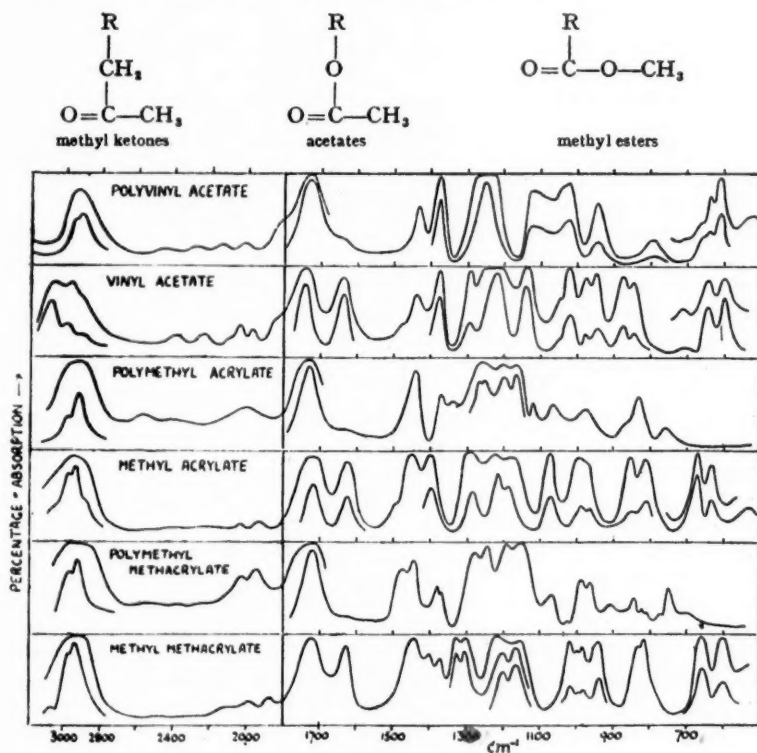
FIG. 3a

concerned with oscillations within the side-chain radicals, and which involve
motions of the weighted carbon chain. In polyvinyl acetate we should expect
the side chains to be —O—C—CH$_3$, and in the acrylates —C—OCH$_3$. We

have, therefore, measured the spectra of a large number of esters and ketones
of which the most important in this connection are those containing one of the
following structures:
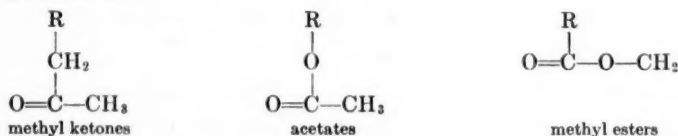
Detailed results will be given elsewhere, but several features are relevant here.
Thus, methyl ketones with the exception of acetone have an intense band at
595 cm.$^{-1}$, whereas other ketones have no analogous band. Acetates have an

intense pair of bands at about 610, 635 cm.$^{-1}$ not found with formates or esters of higher fatty acids. These low frequencies are presumably connected with motions of the

$$C—C—CH_3 \quad \text{or} \quad O—C—CH_3$$
$$\overset{\|}{O} \qquad\qquad \overset{\|}{O}$$
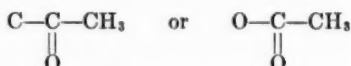
skeleton. Formates have an extremely intense absorption at about 1200 cm.$^{-1}$, which is paralleled in the acetates by a band at 1245 cm.$^{-1}$, and these vibrations are probably controlled by a motion within the skeleton O=C—O—C. There is a similar strong band with many alkyl ethers[9] at 1120–1140 cm.$^{-1}$, and with some aryl alkyl ethers and anhydrides at about 1240 cm.$^{-1}$, so that this region of absorption may be associated mainly with the —C—O—C— part of the skeleton, modified in some cases by the contiguous carbonyl group.

Polyvinyl acetate has bands at 610, 635 cm.$^{-1}$ associated with the acetate side chains; in agreement with the above, polymethyl acrylate and methylacrylate show no such bands in this region. All these polymers show intense absorption in the region of 1150–1250 cm.$^{-1}$, since all have the modified ether linkage. This region of absorption is more complex with the acrylates than with polyvinyl acetate, and it is worth noting here that the same result is found with methyl esters of higher fatty acids, which would be expected on the basis of structure to be more closely analogous to the acrylate polymers with the structure, R—C—OCH$_3$. All the polymers show the characteristic carbonyl

$$\overset{\|}{O}$$

group absorption at 1720–1730 cm.$^{-1}$ and the deformational vibration of methyl groups at about 1375 cm.$^{-1}$. In polyvinyl acetate this latter band seems relatively more intense than with the acrylates; in the former case the methyl group is attached to carbon and contiguous to the carbonyl group, and in the latter it is attached to oxygen. In polymethyl methacrylate the band due to the methyl group deformation seems to split, with components at 1370 and 1380 cm.$^{-1}$; this polymer contains two kinds of methyl group, whereas the other two polymers contain only one. The bands at about 1445 cm.$^{-1}$ are connected with CH$_2$ group deformations, and that at 1480 with polymethyl methacrylate may also arise from another unsymmetrical CH$_3$ group deformation which is absent with the other two polymers. There are some interesting differences with these polymers in the frequencies of the C—H stretching vibration bands between 2900–3000 cm.$^{-1}$. All the polymers show a feeble band at about 1630 cm.$^{-1}$; whether this is due to the presence of residual monomer, or to some unexpected type of condensation, is not clear.

Condensation of vinyl acetate may lead to skeleton units of the type:

$$—CH_2—CH——CH_2—CH— \qquad —CH_2—CH————CH—CH_2—$$
$$\qquad | \qquad\qquad | \qquad\qquad\qquad | \qquad\qquad\qquad |$$
$$\qquad O \qquad\qquad O \quad\text{or}\quad\qquad O \qquad\qquad\qquad O$$
$$\qquad | \qquad\qquad | \qquad\qquad\qquad | \qquad\qquad\qquad |$$
$$O=C—CH_3 \quad O=C—CH_3 \qquad O=C—CH_3 \quad O=C—CH_3$$
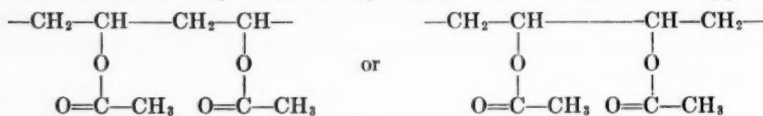
and condensation of methyl acrylate to

$$—CH_2—CH——CH_2—CH— \qquad —CH_2—CH————CH—CH_2—$$
$$\qquad | \qquad\qquad | \qquad\text{or}\qquad\qquad | \qquad\qquad\qquad |$$
$$O=C—OCH_3 \quad O=C—OCH_3 \qquad O=C—OCH_3 \quad O=C—OCH_3$$
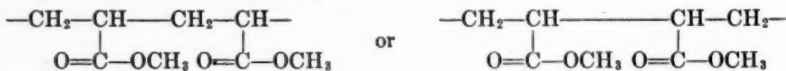
For reference, the spectra of compounds such as diacetyl glycol, diacetyl trimethylene glycol, isopropyl acetate, methyl isobutyrate and methyl succinate, are required. A number of these compounds have been examined, but the

data are still not complete enough to provide unambiguous conclusions. On the other hand there is a marked parallelism between the spectra of polyvinyl acetate and isopropyl acetate (Fig. 3b), and a far greater similarity between
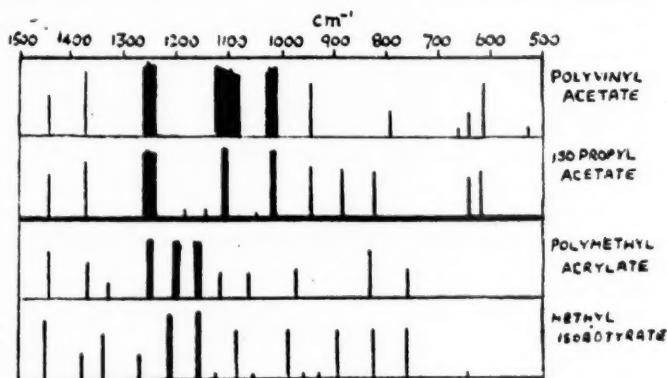
Fig. 3b

those of polymethyl acrylate and methyl isobutyrate than between that of polymethyl acrylate and any other relevant esters which have been measured. This may imply that the predominant type of condensation is head to tail.

Similar comparisons have been made between the spectra of polyvinyl and polyvinylidene chloride and those of simple chlorinated paraffins; and some structural correlations have been deduced. Here too, however, more reference data are required. A related problem arises with the halothenes made by chlorination of polythene. Continued chlorination leads to well-marked changes in the spectrum (Figure 4). Thus, as the percentage of chlorine in-
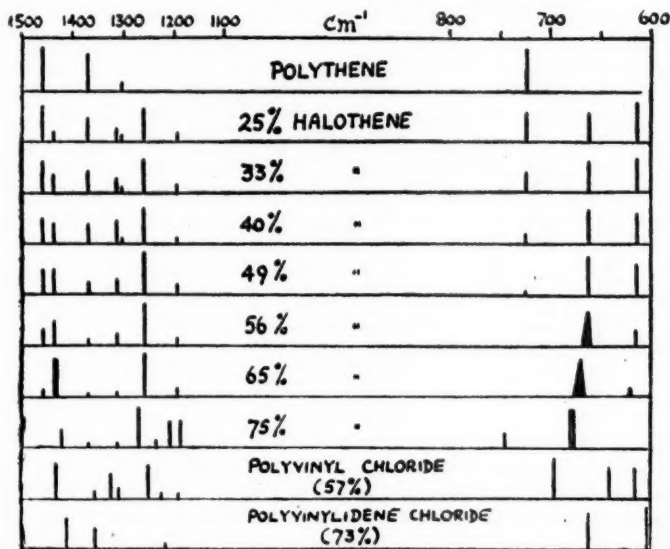
Fig. 4

creases, the band at 722 cm.$^{-1}$ connected with the long carbon-carbon chain
vibration diminishes in intensity, and when about 50 per cent of chlorine by
weight is present this band has entirely disappeared.   This band is known to
appear with chains of four or more carbon atoms.   Taken together these facts
give some suggestions about the distribution of chlorine atoms along the chain,
but allowance must be made for the simultaneous chlorination of the methyl
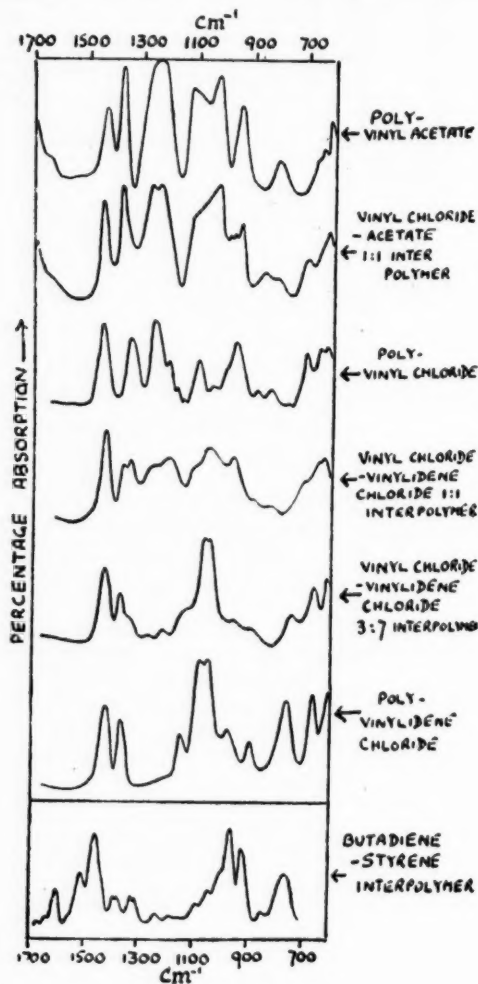
FIG. 5

groups.   The band at 1375 connected with the methyl groups also weakens as
the chlorination proceeds, and that at 1460 cm.$^{-1}$ associated with a CH_2 group
deformation also weakens slowly.   As with simple chlorinated paraffins this
methylene group deformation is lowered if a chlorine atom is attached to a
neighboring carbon atom, and in the halothenes bands appear at 1440 cm.$^{-1}$
and lower frequencies in addition to that at 1460 cm.$^{-1}$.   The latter disappears

when the percentage of chlorine is such that there are effectively no undisturbed methylene groups. From correlations with the spectra of simple chlorinated paraffins it may be possible to get more exact ideas about the distribution of chlorine atoms along the carbon chain. It is interesting to notice that the vibrational spectra of polyvinyl chloride and polyvinylidene chloride are different from those of halothenes with the same percentage of chlorine by weight.

The infrared spectra of Neoprenes—polychloroprenes—also reveal differences in samples made under different conditions of polymerization, and although the structural differences have not yet been fully elucidated, it is useful from the theoretical side to compare the course of the polymerization of chloroprene with that of butadiene, isoprene or similar substances.

Other features of interpolymerization can also be conveniently studied in this way. When, for example, butadiene and a vinyl derivative such as styrene or acrylonitrile form an interpolymer, it may be desirable to have a quick and certain method for the estimation of the proportions of the components which are combined in the product. With Buna-S, a butadiene-styrene interpolymer, phenyl groups can be estimated from their absorption at 760 cm.$^{-1}$, and with butadiene-acrylonitrile polymers, such as Perbunan, Hycar, or Butaprene, the cyanide group can be estimated from the band at about 2250 cm.$^{-1}$. At present the main experimental difficulty in this work is the preparation of films of known thickness, and it may be necessary in practice to use an internal standard for control of this, such as the absorption of some characteristic unit, such as a methylene group. If in some interpolymerization process, each component polymerizes independently, the separate polymers can often be detected in the final mixture by means of their characteristic absorption bands. When varying amounts of propylene are allowed to polymerize with ethylene in the formation of a polythene, the take-up of propylene can be followed by the absorption of the bands due to methyl groups, as well as by changes in the spectrum of the product. The spectra of some typical interpolymers are shown in Figure 5.
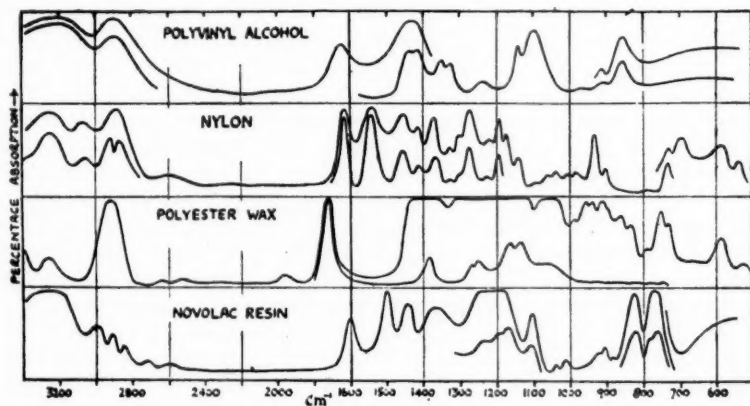
Fig. 6

The spectra of other compounds of high molecular weight are shown in Figure 6. There are two important differences between that given here for polyvinyl alcohol and the curve given by Barnes, Liddel and Williams[10]. These workers found two fairly strong bands at 1240 and 1740 cm.$^{-1}$, which

must have been due to acetate groups remaining in a product made by the hydrolysis of polyvinyl acetate. The band at 1740 cm.$^{-1}$ due to carbonyl groups is not detectable in our curve, but the feeble band at about 1240 cm.$^{-1}$ may imply a small amount of polyvinyl acetate impurity. As explained above, this is the most intense band in the spectra of acetates. Although polyvinyl alcohol has relatively few absorption bands, correlation with the molecular structure is difficult. Comparisons have been made with the spectra of ethyleneglycol, isopropyl alcohol, trimethyleneglycol, butane-1,4-diol and similar substances. The results are not very convincing, though there is some similarity with isopropyl alcohol, which might imply the structure:

$$-CH_2-CH-CH_2-CH-$$
$$\qquad \quad | \qquad \qquad |$$
$$\qquad \quad OH \qquad \quad OH$$
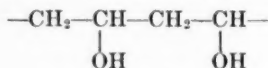
On the other hand, the similarity with trimethyl glycol is not so obvious. The band at about 1100 cm.$^{-1}$ with polyvinyl alcohol is certainly connected with the hydroxyl group, and that at about 1430 cm.$^{-1}$ with a deformation of C—H bonds. The broad region of absorption from about 700 cm.$^{-1}$ to lower frequencies has been found with other oxygenated hydrocarbons and some oxidized hydrocarbon polymers; its exact significance is unknown, but methyl alcohol has a broad absorption band in this region. Other features suggest that a small amount of residual water was present in the sample of polyvinyl alcohol, which was a film made by evaporation of an aqueous solution from a heated glass plate. Thus the band at about 1650 cm.$^{-1}$ might be due to adsorbed liquid water; if it were connected with a C=C bond formed by loss of water during the heating in preparing the film, we should expect to find another strong band due to the olefinic part of the skeleton formed, probably at 965 cm.$^{-1}$, and none is observed. The broad band between 3000–3400 cm.$^{-1}$ seems to imply some O–H interaction such as hydrogen bonding, though here, too, the true spectrum may be masked by residual water.

Nylon-66 has also been measured, not only because of its intrinsic importance, but also in relation to other work on the infrared absorption of amides, amino acids and proteins. The most striking feature of the spectrum is the displacement of the carbonyl group band from its usual position at 1720–1740 cm.$^{-1}$ to about 1630 cm.$^{-1}$. This occurs with amides in general[11], and must arise from some form of interaction between the carbonyl and NH groups. Several interpretations have been discussed. In the case of Nylon, hydrogen bonding of the type —C=O——H—N— may be formed by interaction between units in different chains or within the same chain. Pauling has suggested that, in the case of amides, resonance may occur between ionic structures localized on the —CO—NH— part of the skeleton. Much of the absorption by Nylon between 1200–1700 cm.$^{-1}$ must be due to vibrations of the —C—CO—NH—C— part of the structure. The broad bands in the region of 3100–3300 cm.$^{-1}$ also suggest that the N—H bonds are subject to interactions or electronic influences which lead to abnormal stretching vibration frequencies. If the bands in the region of 3μ and 6μ are examined in greater detail it may be possible to get more information about this molecule.

A comparison of the spectra of polyesters and polyester amides with that of Nylon is also interesting. With Nylon, a condensate from adipic ester and hexamethylenediamine, there is the fundamental unit:

$$-CO(CH_2)_4-CO-NH-(CH_2)_6-NH-$$
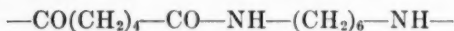
In the polyesters, such as that formed from adipic ester and ethyleneglycol, there is the unit:

$$-CO(CH_2)_4-CO-O-(CH_2)_2-O-$$
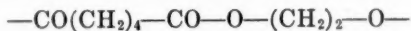
In this case the carbonyl frequency is found at its normal position, and there is the customary intense ester band at 1100–1200 cm.$^{-1}$. Here, too, the bands in the region of 3000–3400 cm.$^{-1}$ connected with C—H stretching vibrations, and possibly with end groups, are informative. Similar points emerge from the spectra of polyester amides, where both the normal carbonyl group frequency and that diminished by an adjacent NH group arise.

Another type of compound which lends itself to infrared examination is that formed by the condensation of a phenol or cresol with formaldehyde. Figure 6 shows the spectrum of a Novolac resin made from phenol and formaldehyde. In this condensation several possible structures can be formed. A simple union of the molecules, with loss of water, may lead to the chain:

I. (chain of phenol rings bearing OH groups linked by —CH₂— groups)
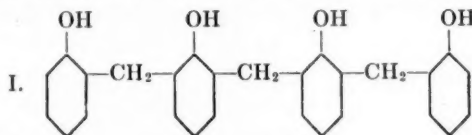
but *para* linking may also occur leading to units such as:

II III IV (structures of hydroxy-substituted benzene rings linked by CH₂ groups)
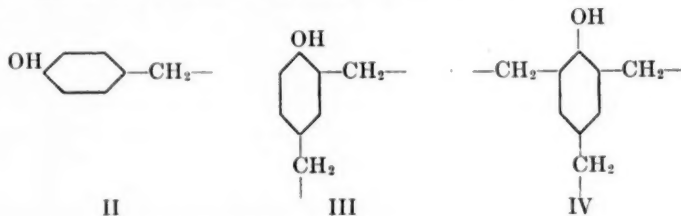
It seemed possible that if reference data were available from the spectra of substances such as cresols, xylenols, hydroxy- and dihydroxydiphenyl methanes, and monoalcohols of the cresols, some structural correlations might be obtained, and this has already been confirmed. Thus, benzene has a very strong absorption band at 671 cm.$^{-1}$ which has been assigned[12] to a vibrational mode involving the motion of the 6-carbon ring as a rigid unit through the plane of the six hydrogen atoms. When a single substituent is attached to benzene, such as OH, NH$_2$, NHCH$_3$, N(C$_2$H$_5$)$_2$, Cl, OCH$_3$, or an alkyl radical, the "benzenoid" frequency shifts to 740–760 cm.$^{-1}$. If two such substituents are present the exact value of this frequency depends not so much on their chemical nature as on their relative position—*ortho*, *meta* or *para*. With *ortho* compounds it is at about 740–750 cm.$^{-1}$, with *meta* at 770–790 cm.$^{-1}$, and with *para* at 810–830 cm.$^{-1}$. The data with xylenols[13] suggested that in trisubstituted benzenes the corresponding vibration still persists, and that its frequency may be determined primarily by the arrangement of the substituents in the 1,2,3-, 1,2,4- or 1,3,5-positions. Comparison with the spectra of other trisubstituted benzenes show that a useful fairly general rule can be set up, that 1,2,3-compounds have an intense band at about 760–770 cm.$^{-1}$, 1,2,4-compounds at 800–815 cm.$^{-1}$, and 1,3,5-compounds at 825–835 cm.$^{-1}$. Although there are some limitations to this rule, the data already suggest some regularities among the radicals which do not conform.

Applying these arguments to the spectrum of the Novolac resin shown in Figure 6, the two bands at about 760 and 820 cm.$^{-1}$ are particularly important. If the resin had contained a simple chain shown above as I, the bands in this part of the spectrum should correspond to those of *ortho* cresol and 1,2,6-xylenol. The "benzenoid" frequency of the former was at about 752 cm.$^{-1}$, and of the latter at about 762 cm.$^{-1}$. Either of these skeleton units could, therefore, account for the Novolac band at 760 cm.$^{-1}$, but some other nuclear structural arrangement must give rise to the band at 820 cm.$^{-1}$. A satisfactory interpretation would be to assume that the resin contains some *para* substituted nuclei, which could either be II or III. Thin solid films of 2-hydroxy-5-methylbenzyl

<div style="text-align:center">

OH   OH

—CH₂OH   CH₃— —CH₂OH

V   VI

CH₃   CH₃

</div>
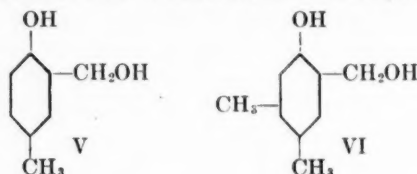
alcohol (V) have a strong band at about 815 cm.$^{-1}$, and the *para* hydroxy diphenyl methanes (2,4' or 4,4') have bands at about 820 cm.$^{-1}$. Groupings of the type IV are probably absent from the resin, since benzene derivatives with 1,2,3,5-substitution have an intense "benzenoid" band at about 850 cm.$^{-1}$, of which the resin shows no sign. Similarly, the 1,2,4,5-skeleton can be excluded, since 2-hydroxy-4,5-dimethylbenzyl alcohol (VI) has the intense "benzenoid" band at 855, 5-ethyl-pseudocumene at 870 and durene at 865 cm.$^{-1}$.

The strong band with the Novolac at 1200 cm.$^{-1}$ is connected with vibrations involving the hydroxyl groups, and other bands can be related to characteristic oscillations of the aromatic nucleus. The broad hydroxylic absorption at about 3300 cm.$^{-1}$ is also informative, but these details are left for detailed consideration elsewhere.

Figure 7 shows the spectra of three typical cellulose materials. Cellulose acetate and acetobutyrate have the carbonyl group absorption at 1740 cm.$^{-1}$, which is absent in the cellulose ether. The latter has a very intense band at about 1100 cm.$^{-1}$, which was connected above with the ether linkage —C—O—C—. Both acetate and acetobutyrate have similar intense absorption between 1000–1250 cm.$^{-1}$ connected with the

$$R_1—\underset{\underset{O}{|}}{C}—O—R_2$$
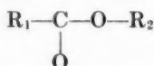
part of the structure. The small differences in this region between the two esters is noteworthy. Cellulose acetate has the strong methyl band at 1375 cm.$^{-1}$, but when butyrate radicals are introduced other C—H deformation frequencies appear at about 1415 and 1460 cm.$^{-1}$. The variations in position and intensity of some of the bands in the region 2800–3600 cm.$^{-1}$ with the different celluloses are very important, since these are connected with C—H and O—H stretching vibrations and from them we may determine residual hydroxyl groups and the extent of hydrogen bonding.

Some general considerations affecting infrared measurements with large molecules must now be mentioned. For example, some of the correlations which have hitherto been made between vibrational spectrum and structure have been arrived at by comparing the spectra of substances in different states of aggregation. Measurements now show that such comparisons must be

made cautiously, for the spectrum of a substance may change very strikingly when it changes its physical state. Displacement of vibration bands on passing from vapor to liquid have long been known, particularly in comparing Raman data for liquids with infrared data on the corresponding vapors; and it is well known that band contours with vapors may be entirely absent with the liquids. The marked changes, both in wave length and intensity, of vibration bands on passing from liquid to solid which have recently been observed with compounds of very different chemical nature are surprising. In the same way the spectrum
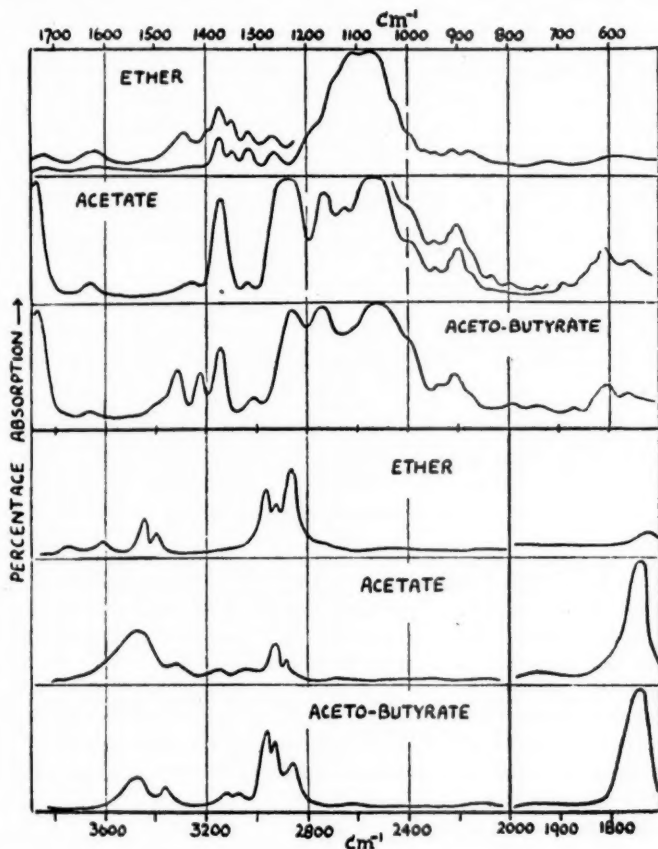
FIG. 7

of a pure liquid has been found to differ from that of a dilute solution in ways which must arise from causes other than intermolecular association or hydrogen bond formation. There are possible theoretical reasons for these changes in both the frequencies and intensities. For example, in the case of a long-chain molecule in the solid state, not only may the potential energy function in the solid lattice become altered on melting, leading to shifts in frequencies, but also the internal molecular shape may change and lead to changes in the selection rules or factors which determine the relative intensities of bands.

Such changes in spectrum with solid and liquid have been found with compounds like the cresols and xylenols, but also with long-chain paraffins. Usually the bands are sharper and more numerous with the solid. The pair of sharp peaks with polythene at about 722 cm.$^{-1}$ becomes a single broad band with liquid polythene waxes, as it is with the lower straight chain paraffins. These changes may have significant implications. For instance, the two feeble bands of polythene at 1080 and 890 cm.$^{-1}$ appear to vary in relative intensity in samples of polythene for which x-ray work has shown different ratios of crystalline and amorphous material. If melting leads to the twisting and interweaving of long chains such differences in the relative intensity of bands may arise.

Another promising line of attack is the use of polarized infrared radiation for the study of oriented long-chain polymers, such as polythene, Nylon, and protein materials. The spectra of the sample with the oriented chains successively parallel or perpendicular to the plane of polarization of the incident radiation, might be expected to show differences from which information could be obtained about the disposition and orientation of polar groups along the chain. Some measurements on this effect have already given promising results.

Again, with rubbery materials, it has been suggested that differences in physical behavior may be related to the proportions of sol and gel in the material. It is, therefore, interesting to compare the spectra of the sol and gel. Unfortunately the experimental difficulties in preparing films of gels suitable for examination are often great.

A more fundamental question is the mathematical treatment of the vibration frequencies of long chains or weighted ring systems. Although some approaches have been made, little progress has so far been achieved. Before any detailed treatment is possible more reference data are required, and the present survey may indicate some ways in which these may be used.

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THE BEHAVIOR OF KETENE TOWARDS OLEFINS AND OLEFINIC PEROXIDES *

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Several groups of workers have shown that diphenylketene adds to both conjugated and unconjugated olefins, including cyclopentadiene, cyclohexene, cyclohexadiene, 2,3-dimethylbutadiene and $\Delta^{\alpha\gamma}$-pentadiene, with formation of cyclobutanone derivatives. The only recorded work, however, on the addition of ketene to olefins is that of Brooks and Wilbert,[1] who showed that it reacts under pressure at 100° with an equimolecular quantity of cyclopentadiene to give the bicyclo [0, 2, 3] heptenone. An attempt has now been made to add ketene to representative monoölefins and unconjugated di- and polyolefins, in the examples of 1-methylcyclohexene, dihydromyrcene and rubber, at temperatures ranging from 20° to 120°, either under pressure with the olefins alone, or with solutions of the olefins in suitable solvents (chloroform, toluene, and ether). Under these conditions, no action occurred except the formation of diketene; when, however, sulfuric acid or, better, zinc chloride was added as a catalyst, a small quantity of a high-boiling liquid was formed, even when the olefin was omitted from the reaction mixture. This liquid was a *compound*, $C_7H_{10}O_3$, derived apparently by reaction of ketene with small quantities of acetone which had been carried over from the ketene generator. Ketene reacts with acetone in presence of sulfuric acid to give the acetate (I) derived from the enolic form of the ketone[2]:

$$CH_2:CO + HO \cdot CMe:CH_2 \rightarrow CH_3 \cdot CO \cdot O \cdot CMe:CH_2 \text{ (I)}$$

Other products obtained by these authors were diketene and a higher-boiling residue which they did not identify. It was probably the compound, $C_7H_{10}O_3$, now isolated. Hurd and Williams[3] have shown that the dimer of ketene can behave as acetylketene and it seems probable that this substance has in the present instance reacted with enolic acetone in the same way as does ketene, with the formation of β-propenyl acetoacetate (II):

$$CH_3 \cdot CO \cdot CH:CO + HO \cdot CMe:CH_2 \rightarrow CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot O \cdot CMe:CH_2 \text{ (II)}$$

Although insufficient ester was separated for complete identification, the above formula is supported by all the available evidence (see Experimental Part).

To test the possibility that olefinic hydroperoxides might be stabilized by acetylation with ketene, the reaction between ketene and Δ^2-cyclohexene hydroperoxide was examined. It proceeded readily at room temperature, but the product was almost entirely Δ^2-cyclohexenyl acetate. At a lower temperature the acetate was accompanied by some peracetate, which would consequently appear to be the primary product of reaction:
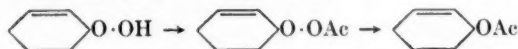
Rubber was not greatly attacked by ketene, but when it was treated concurrently with oxygen and ketene it broke down oxidatively much more rapidly than when treated with oxygen alone, the percentage of oxygen absorbed after 12 hours being 1.7 and 0.2, respectively.   This also would seem to indicate the greater instability of the peracetate groups.

EXPERIMENTAL

(Microanalyses were carried out by W. T. Chambers and (Miss) H. Rhodes)

Interaction of Ketene and Acetone.—Ketene (15 g.) as obtained from the generator[4] contained a little acetone; it was passed into dry ether (30 cc.) at −60°.   After addition of zinc chloride (0.3 g.) as catalyst, the solution was heated in a sealed tube for 4 hours at 100°.   The bulk of the ether and unchanged ketene were then removed, benzene (40 cc.) was added, and the zinc chloride was extracted with water.   After removal of solvent, fractionation of the product gave diketene and a liquid (about 1 g.), b.p. 40°/0.03 mm., $n_D^{18°}$ 1.4632 (Found: C, 59.1; H, 7.2. $C_7H_{10}O_3$ requires C, 59.15; H, 7.0%).

The product dissolved to a slight extent in water, so forming a faintly acid solution which gave a red color with ferric chloride, and in aqueous alcohol it rapidly reduced alkaline potassium permanganate.   The iodine value[5] was 38 after 1 hour and about 190 after eighteen hours ($C_7H_{10}O_3$ |⁻ requires I.V. 89.4). Attempted preparation of the oxime gave only an oil, and condensation with dinitrophenylhydrazine in alcoholic sulfuric acid solution gave acetonedinitrophenylhydrazone, the acid conditions of reaction leading to hydrolysis of the ester; this observation corresponds exactly to that of Gwynn and Degering[2] with the β-propenyl acetate obtained from ketene and acetone.   The derivative, after chromatography in benzene solution through alumina, crystallized from 95% alcohol in orange plates, m.p. 125°.   The dinitrophenylhydrazone prepared from pure acetone and a mixture of the two also melted at 125° (Found: C, 45.5; H, 4.3; N, 23.6.   Calc. for $C_9H_{10}O_4N_4$: C, 45.4; H, 4.2; N, 23.5%).

Absorption spectra: In water, a band (ϵ = 8500) at $\lambda255$.   In cyclohexane, a band (ϵ = 10,000) at $\lambda240$.   The absorption in aqueous solution was unchanged by addition of acid or alkali.

Interaction of ketene and Δ²-cyclohexene hydroperoxide.—To the hydroperoxide[6] (3.7 g.) in toluene (5 cc.) at −70° was added a solution of ketene (2 g.) in toluene (30 cc.) at the same temperature.   The mixture was allowed to warm slowly, and the temperature eventually rose to 45°.   After removal of the residual ketene and toluene, the product (2 g.) was distilled at 27–30°/0.003 mm.   This liquid contained only 0.75% of peroxide and consisted almost entirely of an acetic *ester*, probably Δ²-cyclohexenyl acetate (Found: C, 67.8; H, 8.55. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6%).

In an attempt to obtained the undecomposed peracetate, the experiment was repeated under carefully controlled conditions.   Ketene was bubbled through a solution of the peroxide (3 g.) in toluene (40 cc.) at −70° for 30 minutes. The solution was then allowed to warm very slowly to 0°, and the reaction mixture was worked up as before.   A peroxide determination at this stage showed that only a third of the original peroxide oxygen remained.   The product consisted mainly of the acetate, b.p. 33–34°/0.05 mm., but a few drops of a liquid, b.p. 55–57°/0.05 mm., were obtained.   This strongly peroxidic material was not pure, but its instability and analysis indicated that it was

mainly Δ^2-cyclohexenyl peracetate (Found: C, 62.4; H, 8.1. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%).

Ketene and Rubber.—(1) Excess of ketene was condensed on sol rubber (1 g.) at $-100°$ in absence of air, and the mixture allowed to warm very slowly to 20°. Swelling of the rubber occurred. Some diketene was formed and was removed under reduced pressure; the product was then washed with acetone and dried in a high vacuum [Found: C, 86.6; H, 11.65; O (diff.), 1.75. Found for the original rubber: C, 87.55; H, 11.8 O (diff.), 0.65%]. Although only 1.1% of oxygen had entered the molecule, the rubber had become insoluble in benzene.

(2) Oxygen was passed through a 1% solution of sol rubber in methylcyclohexane for 2 hours, and this was followed by the passage for 10 hours of oxygen and ketene. Ketene, diketene, and the solvent were removed under reduced pressure, and the rubber was dissolved in benzene before precipitation by alcohol [Found: C, 85.9; H, 11.75; O (diff.), 2.35; M (viscosity), 31,000. Found for the original rubber: C, 87.55; H, 11.8; O (diff.), 0.65%; M (viscosity), 230,000]. Under similar conditions, but with the omission of ketene, a product was obtained [Found: C, 87.35; H, 11.75; O (diff.), 0.9. Found for the original rubber: C, 87.4; H, 11.9; O (diff.), 0.7%].

SUMMARY

Ketene will not react additively with unconjugated olefins such as 1-methylcyclohexene, dihydromyrcene, and rubber. Zinc chloride or sulfuric acid promotes reaction of ketene with acetone (carried over from the ketene generator), with the formation of a compound, $C_7H_{10}O_3$, probably β-propenyl acetoacetate. Ketene acetylates olefinic hydroperoxides, but the resultant peracetates are very unstable.

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SOME INFRARED STUDIES ON THE VULCANIZATION OF RUBBER *

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The two most effective ways of altering the physical and mechanical properties of natural rubber are vulcanization[1] and the addition of carbon black. There is, however, little understanding of the structural changes brought about by these processes, in spite of extensive research by chemical and physical methods. For instance, in vulcanization it is not yet decided how the sulfur atoms are incorporated in the rubber polymer, what proportion are in bridges formed between the isoprene chains, whether such bridges are formed by —C—S—S—C— or —C—S—C— links, whether one double bond is broken for each sulfur atom incorporated, and so on. An ancillary problem is the effect of certain "accelerators" on the speed of vulcanization, about which even less is known. Again in the case of reinforcement of rubber by materials such as carbon black, there is controversy on the structural relationship of the carbon black and the rubber. Until such structural problems have been solved on the molecular scale there is little hope of controlling the macroscopic properties of rubber compounds in a truly scientific manner. This paper gives a preliminary account of the application of infrared spectroscopy to some of these problems.

The spectra of the following types of materials have been obtained with a prism spectrometer of good resolving power between 2 and 18μ:

(1) natural rubber
(2) natural rubber + sulfur $\Big\}$ before
    natural rubber + sulfur + accelerators $\Big\}$ "curing"
(3) Same as (b) after "curing" for various periods
(4) natural rubber + carbon black + sulfur + accelerators (uncured and cured)

The results are described in sections corresponding to this classification. The rubber and rubber compounds were generally examined in the form of thin films (approximately 1/20 mm. thick) which were evaporated from benzene solution on clean glass or water surfaces. In a few cases the films were cut from bulk material using a microtome.

The spectrum of natural rubber.—The infrared absorption spectrum of natural rubber has been investigated by several authors[2], who have covered the range from 1 to 14μ. In the present work the spectrum has been examined between 2 and 18μ, with improved resolving power. Figure 1 shows a percentage absorption curve for a thickness of rubber of 0.05 mm., and is in good agreement with the earliest spectrum recorded, *viz.*, that due to Stair and Coblentz. Increased resolving power has enabled us to establish some of

their weaker bands more definitely; we have also detected a new weak band at 4.98μ.

Agreement with the results of some of the other authors cited above is less satisfactory, but, when due allowance has been made for possible errors in wave length determination, the remaining differences can all be accounted for by oxidation which gives rise to intense new bands at approximately 3.0, 5.8 and 9.75μ. These additional absorptions have been found by Stair and Coblentz in the spectrum of heavily oxidized rubber, and have been confirmed by other work in this laboratory[3].

In addition to the band at 4.98μ the present work has revealed a new wide absorption band in the rubber spectrum extending from 16.6 to 17.7μ.
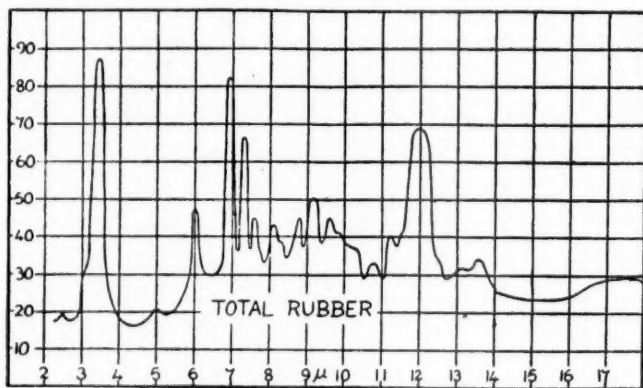
Fig. 1.—The infrared spectrum of natural rubber containing small amounts of proteins, fatty acids, etc.

Spectra of uncured natural rubber mixes containing sulfur and various accelerating agents.—Rubber may be vulcanized by heating (curing) with sulfur alone, but the time required is greatly reduced and the properties of the vulcanized material improved by the addition of small quantities of various materials[4]. Accelerators may be of the basic oxide type, *e.g.*, litharge and lime, or of the organic type, *e.g.*, mercaptobenzothiazole and Santocure. It is also found that zinc oxide acts as an activator for the organic accelerator. Furthermore, stearic acid is known to enhance the activity of zinc oxide when the latter is acting as an accelerator activator. The compositions of the first series of mixes investigated are shown in Table I, chosen to cover the most important cases just enumerated. The spectra of the first and last of these mixes are shown in Figure 2.

TABLE I

(Mixes are conventionally described as x parts by weight of added material per 100 parts of natural rubber)

Mix Number	Rubber	Sulfur	Zinc oxide	Stearic acid	Santocure
A1	100	10	—	—	—
A2	100	10	5	2	—
A3	100	3	5	—	1
A4	100	3	5	2	1

Comparison of these spectra with those of pure natural rubber (Figure 1) and of mixes A2 and A3 (not reproduced) revealed the following facts:

(1) The presence of sulfur in unvulcanized rubber causes no new bands in the rubber spectrum;
(2) The presence of Santocure causes a new band to appear at 13.3μ.
(3) The presence of stearic acid with sulfur and associated accelerators causes a new band to appear at 6.52μ.
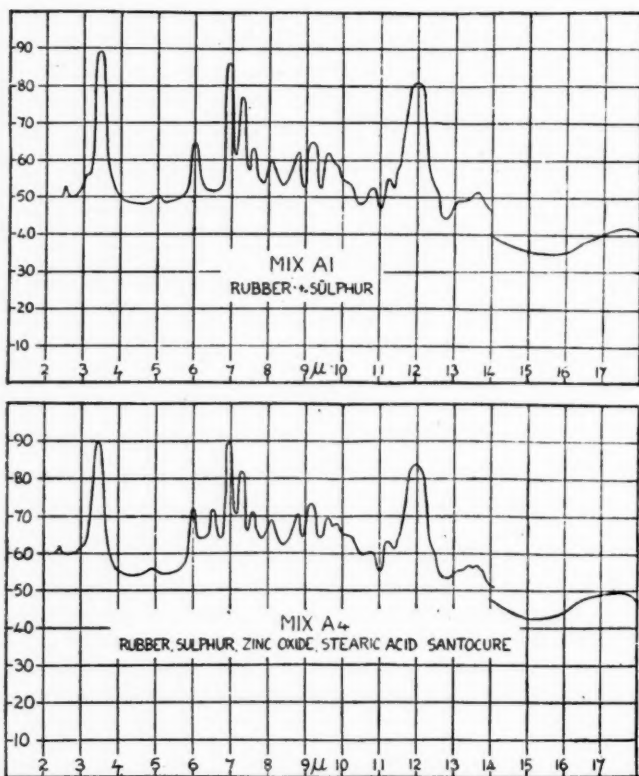
Fig. 2.—The infrared spectra (1) of a "straight" sulfur mix containing 10 parts of sulfur, (2) of an accelerated mix containing 3 parts sulfur, 2 parts stearic acid, 5 parts zinc oxide, and 1 part Santocure. In Fig. 2b the band at 13.4μ should have been drawn at 13.3μ.

The first two results are what one would normally expect from the spectra of the mixtures since sulfur has no bands sufficiently strong to appear at this concentration[5], and in the spectrum of Santocure (Figure 3) the strongest band is at 13.3μ. The third result is of considerable interest since stearic acid (Figure 4a) has no band in this region. To try to settle the origin of this new band the series of mixes given in Table II was made up and examined. The results are shown in column 7 of the table, which lists the intensity of the 6.52μ band relative to any of the moderately intense rubber bands as a standard. They are also illustrated in Figure 5.
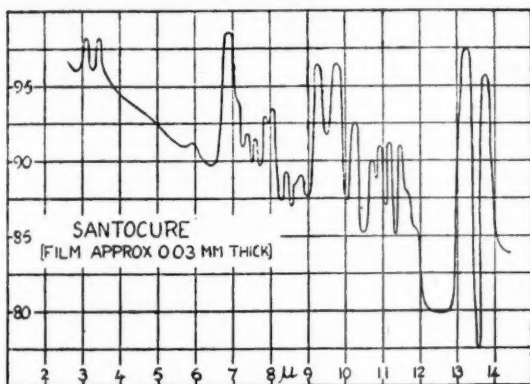
Fig. 3.—The infrared spectrum of a solid film of the organic accelerator, Santocure.
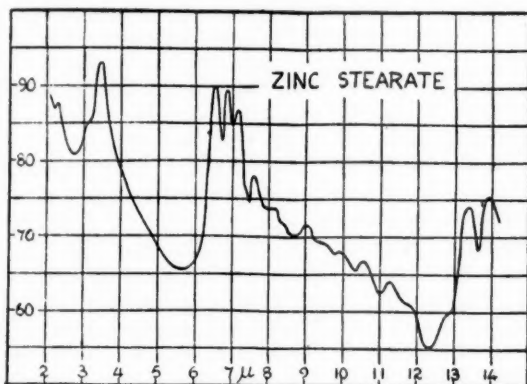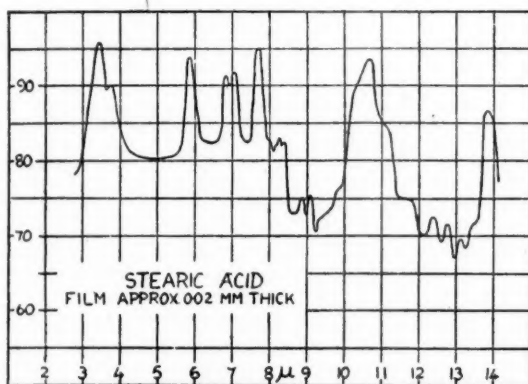
Fig. 4.—The infrared spectra of solid films of (1) stearic acid (2) zinc stearate.

TABLE II

Mix Number	Rubber	Sulfur	Zinc oxide	Stearic acid	Santocure	Strength of 6.52μ band
B1	100	3	—	—	—	—
B2	100	—	5	—	—	—
B3	100	—	—	—	1	—
B4	100	—	—	2	—	weak
B5	100	—	—	5	—	medium
C1	100	—	—	2	1	weak
C2	100	3	—	2	1	weak
C3	100	—	5	2	—	strong
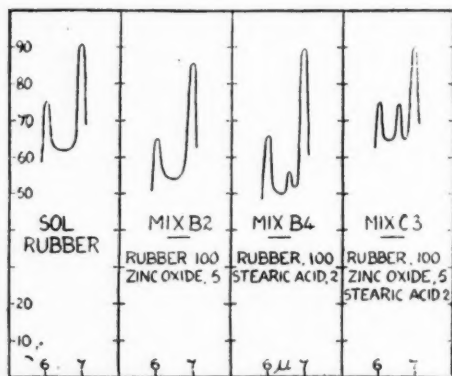
FIG. 5.—Spectra to illustrate the connection of the 6.52μ band with the presence of stearic acid.

The following conclusions may be drawn:

(1) The 6.52μ band is due to some interaction between stearic acid and "rubber", since the presence of added materials is not necessary for its appearance (Mixes B4 and B5).

(2) Since the intensity of the 6.52μ band is enhanced only by the presence of zinc oxide (Mix C3), either the interaction between "rubber" and stearic acid is one which is increased by zinc oxide, or zinc oxide plus stearic acid (which presumably form zinc stearate) give a band in the same position. Mix B2 shows that zinc oxide alone does not give rise to the band.

The possibility of the band being due to zinc stearate was next tested by doing the spectrum of this substance. A very intense band was found in the same position (6.52μ) (Figure 4b); this is in fact the most intense band in the spectrum of zinc stearate apart from bands which are characteristic of the CH vibrations and so overlap intense rubber bands. There are, therefore, strong reasons for associating the 6.52μ band with the presence of stearate ions but this will be more fully discussed later.

Spectra of vulcanized rubber mixes.—We shall report here only the work on Mixes A1 and A4 after curing. These are representative of the two extremes in vulcanizing technique, the former being a "straight" mixture of rubber and sulfur, the latter containing, in addition to sulfur, an accelerator (Santocure) and accelerator activators (zinc oxide and stearic acid). The spectra are shown in Figures 6a and 6b.

Comparison of the spectra of these vulcanized rubbers with the spectra of corresponding uncured mixes (Figures 2a and 2b) reveals new bands in the

vulcanized rubbers at 10.4μ and 17.0μ. The latter is very weak but seems to be above experimental error in the case of cured Mix A1 (Figure 6a). The 10.4μ band has been reported previously by Sears[6]. In addition to the new bands it is important to notice that the 6.52μ band arising from the presence of stearic acid in Mix A4 has disappeared on curing as also has the Santocure band at 13.3μ.
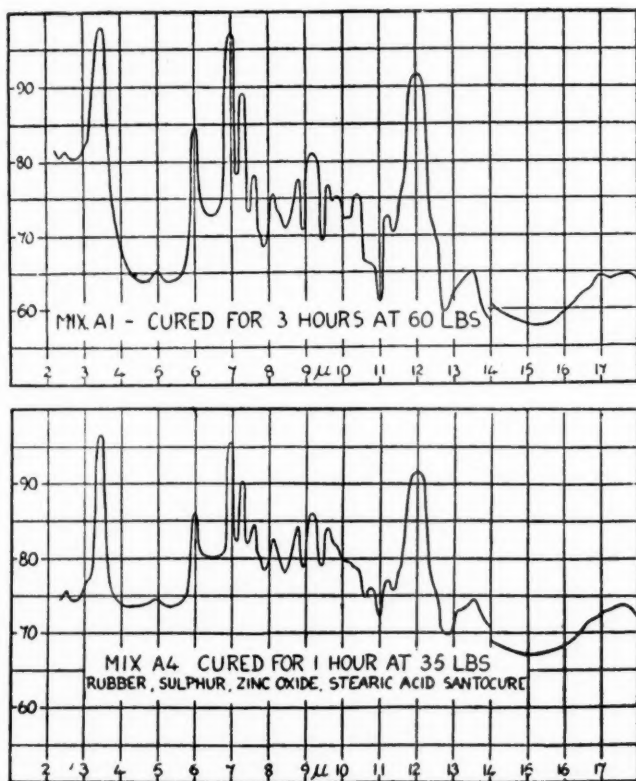
FIG. 6.—The infrared spectra of cured films of (1) Mix A1 cured for 3 hours at 60 lbs. per sq. in. steam pressure (145° C) and (2) Mix A4 cured for 1 hour at 35 lbs. per sq. in. steam pressure (127° C).

It is interesting to note that the 6μ band of natural rubber shows no alteration in intensity other than a possible slight increase. The absolute intensity of this band is hard to determine, since it occurs in a region of intense atmospheric absorption, due to water vapor, but in these mixes and for these times of curing it certainly does not decrease in intensity. There are in fact no appreciable diminutions in any of the bands of rubber on light vulcanization.

Spectra of rubbers containing carbon black.—We report here the results on a mix of the A4 type, (1) containing 5 parts of carbon, before curing; (2) containing 26 parts of carbon, after curing. The spectra are shown in Figures 7 and 8. Considering first the spectrum of the rubber mix containing 5 parts of carbon (Figure 7) we see that nowhere is the absorption less than 75 per cent, and that this background of continuous absorption increases rapidly on passing

to shorter wave lengths. This is an effect which is always present when finely powdered materials are studied in the infrared region of the spectrum, and is due to scattering of the incident radiation by the particles present—in this case by the carbon particles. Such "Rayleigh" scattering is well known to increase in passing to shorter wave lengths. A comparison of the bands superimposed on the scattering background in Figure 7 with the spectrum of the carbon free
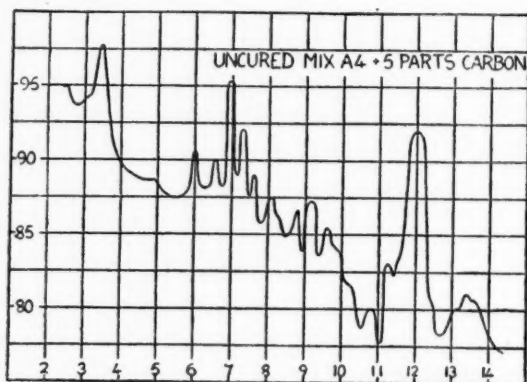
FIG. 7.—The infrared spectrum of an uncured accelerated mix (A4) with 5 parts of carbon.
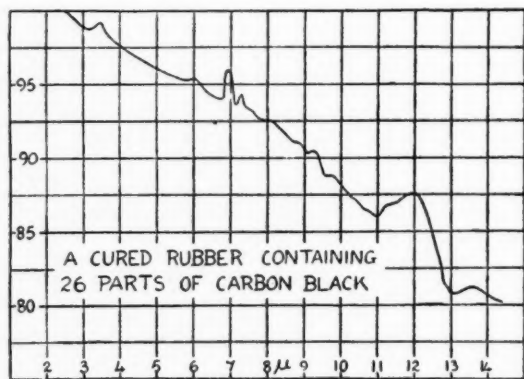
FIG. 8.—An "absorption" curve for a very thin microtome cut film of a cured rubber containing 26 parts of carbon, showing weak rubber absorption bands superimposed on a general scattering background.

Mix A4 shows nothing new. The comparison of intensities is less certain because the scattering effect militates against accurate measurements, but there would seem to be no changes which are not within experimental error.

Although the addition of approximately 5 per cent carbon might be expected to show at least some first signs of any new or changed frequencies, it was thought advisable to check the work with a rubber containing at least twenty parts of carbon, especially as such heavy loadings are used in practical rubber compounding. It was found, however, that such a rubber gave virtually no transmission in the usual thicknesses we had employed (presumably due to the

increased scattering by the carbon black). It was, therefore, necessary to develop a microtome technique of cutting extremely thin films of vulcanized rubber.

The spectrum of such a film is shown in Figure 8. It is obvious that the effective thickness of rubber in the path of the radiation is now much too small. Nevertheless the characteristic rubber spectrum can just be distinguished above the scattering background. Although intensities cannot be measured with any degree of accuracy, it would not appear that carbon affects the gross structure of the infrared spectrum of rubber (vulcanized or unvulcanized) to any appreciable extent.

DISCUSSION

At present the infrared spectrum of rubber, like that of any polymer, can only be partially interpreted. Following the general rules for such spectra[7] we have the following assignments:

Class	Wave length in μ	Detailed interpretation
Hydrogen Frequencies	3.4	ν_{CH} valency
	6.9	δ_{CH} deformation (CH_2 and CH_3 groups)
	7.3	δ_{CH} deformation (CH_3 group)
Double bond Frequencies	6.0	$\nu_{C=H}$ valency

None of the other bands in rubber can yet be assigned with any degree of certainty, although it is probable that the weak band at 2.5μ is a combination band arising from the transitions to levels of the type $\nu_{CH} + \delta_{CH}$. The weak band near 3.0μ was at first assigned to ν_{OH}, the hydroxyl presumably arising from slight oxidation. More recent work indicates that this band is separate from the oxidation band at 3.0μ and its wave length is 3.1μ. It now seems more probable that it is either a weak combination band or a CH fundamental frequency. If the latter is true, it would indicate the existence of a CH group in rubber in which the CH distance is about 1.06 A, $i.e.$, virtually the same as that found in C_2H_2 (1.057 A)[8] and HCN (1.06 A)[9], and considerably less than that found in methane (1.093 A)[10] and ethylene (1.085 A)[11]. This may be the CH distance of the "long" hydrogen on the ethylene bond. Thus, although the part of the infrared spectrum which arises from the skeletal vibrations of the isoprene chains, $i.e.$, from 7.5 to 18μ, cannot yet be interpreted, we have in the short wave region "tracer" bands which should make it possible to follow changes which vulcanization may cause in C—H and C=C bonds.

The stearic acid band at 6.52μ.—This is the only band appearing in the spectrum of rubber mixes before curing which is not due to the separate components of the mixture. Since it coincides with an intense band in zinc stearate and is intensified when zinc oxide accompanies the stearic acid, the natural deduction is that this band is due to the stearate ion. The stearate ion would be expected to have a frequency very close to this value arising from the unsym-

metrical valency vibration of the $\left[\begin{array}{c} O \\ C \\ O \end{array} \right]^{-}$ ion[12] while potassium stearate[13] has

been found to have an intense band at 6.45μ. However, if we accept this interpretation, it is difficult to explain how the stearic acid comes to be ionized

in rubber before the addition of zinc oxide. Furthermore natural rubber generally contains 1–2 per cent of carboxylic acids and, therefore, the addition of zinc oxide to rubber might be expected to produce

$$\left[X{-}C{\Big\langle}\begin{matrix} O \\ O \end{matrix} \right]^{-}$$

ions which should give the 6.52μ band. The fact that zinc oxide in rubber does not give rise to the band can, of course, be accounted for if we suppose that more than 2 per cent of

$$\left[X{-}C{\Big\langle}\begin{matrix} O \\ O \end{matrix} \right]^{-}$$

ions are necessary to make the band detectable.

Further quantitative work is required to resove these difficulties. Meanwhile there is definite spectroscopic evidence that zinc stearate is formed when zinc oxide and stearic acid are added to rubber before vulcanization, and that this zinc stearate is destroyed as vulcanization proceeds.

It should perhaps be added that we also have evidence that when stearic acid is added to rubber some of it remains unaltered, since it can be detected by means of its characteristic carbonyl band near 5.8μ.

Changes in the spectrum produced by vulcanization.—Before discussing the new bands at 10.4 and 17μ, it is useful to consider what changes in the spectrum might have been expected, according as the sulfur is incorporated in different ways. Spectroscopically the new bond easiest to detect would be the S—H bond, which would give a band very close to 3.9μ. No trace of such a band has been found, so we may rule out the formation of thiols in vulcanization. If —C—S—C— linkages are formed, a rough calculation shows that the associated new bands lie beyond 13μ; if —C—S—S—C— linkages are formed the S—S bond should be distinguishable from the C—S bond, but it would be expected to give a band beyond 20μ. If C=S bonds are formed one may expect the corresponding valency vibration to become active in the region between 6.5 and 15μ. Until much more work has been done on the spectra of sulfur-hydrocarbon compounds of known structure, it will not be possible to say whether any carbon-sulfur bonds detected occur in a chain or in a ring structure. Finally we may look for changes in the original rubber spectrum. Thus if sulfur is incorporated at the expense of C=C double bonds, we may expect a diminution in the intensity of the 6μ band, while any alteration in the ratio of CH$_2$ to CH$_3$ groups will be reflected in a corresponding alteration in the relative intensity of the 6.9 and 7.3μ bands associated with these groups.

With these considerations in mind the simplest interpretation of the new bands at 10.4 and 17μ is that the former is due to C=S bonds and the latter to C—S bonds. Unfortunately the simplest interpretation is not necessarily the correct one, but it does seem probable that the 17μ band arises from C—S bonds. In dimethyl sulfide, Thompson[14] has assigned the two C—S valency vibrations to frequencies at 691 and 742 cm.$^{-1}$. When the methyl groups are replaced by carbon chains, these frequencies might be expected to be altered sufficiently for one of them to move to 17μ. No infrared data exist on organic sulfides for the region beyond 16μ but the Raman spectrum of diallyl sulfide[15]

shows a frequency corresponding to an infrared absorption at 16.9μ. We are hoping to examine shortly the spectra of a number of organic sulfides and so confirm this assignment.   Since C=S bonds are unlikely on chemical grounds, the next simplest spectroscopic interpretation of the 10.4μ band is that it derives from a combination of the —C—S—C— deformation frequency with one of the C—S valency frequencies of the same group.   It might, however, be purely a frequency of the carbon part of the molecular framework which has become "active" through the alteration of symmetry caused by the introduction of a sulfur atom into the framework.   Here again further fundamental work on simpler molecules of known structure is required.

Probably the most interesting spectroscopic result so far derived is the negative one that the intensity of the C=C band at 6μ is not altered by vulcanization with 10 parts of sulfur unless perhaps to be somewhat intensified. A number of other vulcanized rubbers have been examined in the course of this work including one containing 33 parts of sulfur.   Even this compound after curing for six hours at 145° C showed only a small decrease in the intensity of the 6μ band.   This does not prove conclusively that the ethylenic linkages are virtually unaffected by vulcanization.   The intensity of the 6μ band is a function of the asymmetry of the groups attached to the carbon atoms at either end of the bond.   If this asymmetry is increased on some double bonds by part of the sulfur, while the rest of the sulfur is compounded by the complete rupture of other double bonds, the intensity of the 6μ band may either increase or decrease according to the relative effects of these two processes.   There is in fact some evidence that the 6μ band increases in intensity at first and subsequently (after long curing with 10 per cent or more sulfur) decreases.   In any case it does seem certain that an appreciable degree of unsaturation remains, even with 33 per cent sulfur and a considerable degree of vulcanization.

Effect of carbon black on rubber spectrum.—It has already been remarked that no new bands are produced by the addition of carbon black, and the only appreciable changes in intensity are those caused by the scattering effect of the carbon particles, which makes the bands appear progressively stronger as we move to shorter wave lengths.   A few measurements have been made to see whether Rayleigh's law is obeyed in these phenomena.   The results indicate that, whereas Rayleigh's law would give:

$$\log I/I_0 = - K/\lambda^4$$

where λ is the wave length of the radiation, I is the intensity of the transmitted radiation, and I_0 is the intensity of the incident radiation, the intensities in our curves obey a law where the index of λ is approximately unity.   The carbon particles in these experiments had a mean diameter of 0.03μ.   One might have expected Rayleigh's law to hold if no aggregation took place since the wave lengths were at least 100 times the size of the particle.   If, however, aggregation took place and the particle size became of the same order as the wave length, then anomalous scattering results.   Pfund[16] has investigated phenomena of this type experimentally and has shown that, when the particle size becomes of the same order as the wave length, a sharp change in the intensity of the scattered radiation is to be expected.   Further work is required on the fundamentals of this subject before accurate quantitative deductions can be made, but we can state that the intensity of the scattered radiation in the infrared indicates that the carbon black in these rubbers aggregates from an initial size to 0.03μ to a particle of the order of 1μ in diameter.   Fuller details of these experiments will be published in due course.

SUMMARY

Infrared absorption spectra have been determined between 2 and 18μ for the following materials: (1) natural rubber; (2) natural rubber + sulfur and (or) various accelerating agents, before and after vulcanization, and (3) natural rubber mixes containing carbon black, before and after vulcanization. The accelerating agents studied were zinc oxide, Santocure and stearic acid. New bands have been detected in natural rubber at 3.1, 4.98 and 16.6–17.7μ. Evidence has been found for the existence of stearate ions in rubber mixes to which zinc oxide and stearic acid have been added. The addition of stearic acid alone to natural rubber also gives rise to a band in the position associated with the stearate ion (6.52μ). The explanation of this phenomenon is not clear. Vulcanized rubber shows two bands at 10.4μ and 17μ not present in uncured rubber. The latter is probably associated with C—S bonds. Vulcanization produces very little effect on the C=C frequency of rubber at 6μ, so appreciable unsaturation would appear to exist in highly vulcanized rubber. Carbon black produces no marked alteration in the spectrum of rubber (vulcanized or unvulcanized) other than effects due to scattering. The variation of this scattering with wave length indicates that the size of the carbon aggregate in rubber is the order of 1μ.

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GENERAL DISCUSSION *

DR. SUTHERLAND (*Cambridge*) said: We have carried out a considerable amount of work on polymers in Cambridge along the same general lines as those described by Thompson and Torkington, and, broadly speaking, our results and conclusions are in agreement with theirs. It was originally planned

* Of the preceding two papers.

that our results should also be presented at this meeting, but pressure of other work has made this impossible. It may stimulate discussion if I indicate a few points on which we differ.

First with regard to the rule for classifying compounds with an ethylenic linkage (which is an extension of an earlier rule given by Lambert and Lecomte[1]) certain diallyl compounds recently investigated by Willis appear to break this rule, e.g., diallyl succinate, which has the 990 cm.$^{-1}$ band but not the 909 cm.$^{-1}$ band. Again, in the course of work on rubber, several compounds have been examined in which the $R_1R_2C = CHR_3$ structure was known to exist, but no strong band was found at 840 cm.$^{-1}$, e.g., trimethylethylene. I feel, therefore, that further work is required to define the exact limitations of this rule before it can be applied with complete confidence.

With reference to the possible existence of CH_3 groups in polystyrene being indicated by the band at 1380 cm.$^{-1}$, I would draw attention to a note by Wright[2] on the short wave region of this spectrum, which proved (using the characteristic bands for CH_3 first established by Fox and Martin[3]) that there cannot be more than one CH_3 group per 100 units in the polystyrene chain.

With reference to the spectra of natural rubber and related compounds, a considerable amount of work has been done here by Harding under the auspices of the British Rubber Producers' Research Association. Interesting differences have been found between the spectra of natural rubber, gutta-percha (the α and β forms of which give different spectra) and synthetic poly-isoprene. With regard to the rubber and gutta-percha, these differences are presumably due to cis/trans isomerism, and a study is now in progress of simpler analogs of these isomers.

As regards the spectrum of polyvinyl alcohol, I would point out that Lecomte[4] has given empirical rules, which are fairly reliable in differentiating between a primary, secondary and tertiary alcohol. The characteristic band of a secondary alcohol, according to Lecomte, is at 1100 cm.$^{-1}$, which would indicate for polyvinyl alcohol the structure:

$$-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-$$
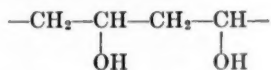
Recent work in Cambridge on alcohols gives general confirmation to Lecomte's rules.

In the case of Nylon, which we have also investigated, I should like to point out that the infrared spectrum gives bands at 3.0 mμ and 6.0 mμ, which might indicate, respectively, the presence of OH and C$=$N bonds, so it is not possible at this stage to exclude groupings of the type:

$$-(CH_2)_6-N=C(OH)-(CH_2)_4-$$
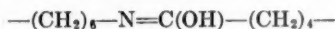
in Nylon.

Mr. D. A. Ramsay (Cambridge) said: The spectra of several polystyrenes have been investigated in the region 2.0–15.0 mμ, of which the rheological properties differed. No significant differences were detected in this region of the spectrum; hence the differences in the rheological properties must be related to structural differences, which do not appreciably influence the infrared spectrum, e.g., variations in chain length rather than chain branching.

A further sample of polystyrene, which from its abnormal swelling properties and anomalous viscosity measurements was believed to be cross-linked, again displayed no differences in this region of the spectrum. Hence it was concluded

that the amount of cross-linking was small. Further work, however, is still required to enable us to determine the minimum amount of cross-linking detectable in polystyrene by the infrared method.

Samples of polystyrene polymerized under various conditions have been examined, but in general the differences observed were very small. A sample of polystyrene polymerized in the presence of 2 per cent benzoyl peroxide catalyst, however, exhibited two new frequencies of appreciable intensity at 1276 cm.$^{-1}$ and 1105 cm.$^{-1}$ which are not due to benzoyl peroxide. Whether these are due to alterations in the polystyrene chain or to the presence of C—O—C linkages is not yet settled.

MR. HARDING (*Cambridge*) said: I should like to draw attention to a particularly interesting result we have obtained from infrared studies of rubber and of synthetic polyisoprene.

In the infrared spectrum between 1300 cm.$^{-1}$ and 700 cm.$^{-1}$, the strongest absorption band of rubber is at 840 cm.$^{-1}$, whereas synthetic polyisoprene has its strongest band at 890 cm.$^{-1}$. A band at the latter position, as Dr. Thompson and others have pointed out, is probably characteristic of the $\begin{array}{c}R_1 \\ \diagdown \\ \diagup \\ R_2\end{array} C{=}CH_2$ grouping. This suggests that the polymerization of isoprene takes place chiefly by 1,2-addition, giving the structure:

$$-CH_2-CH-\vdots\, CH_2-CH-\vdots\,-$$
$$\begin{array}{cc} \mathrm{C-CH_3} & \mathrm{C-CH_3} \\ \| & \| \\ \mathrm{CH_2} & \mathrm{CH_2} \end{array}$$
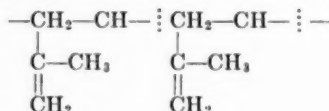
A weak band in synthetic polyisoprene at 840 cm.$^{-1}$ indicates that there may be some 1,4-addition in the polymerization, giving the normal rubber structure:

$$\begin{array}{cc} \mathrm{CH_3} & \mathrm{CH_3} \\ | & | \\ -\vdots\,-CH_2-CH{=}C-CH_2-\vdots\,CH_2-CH{=}C-CH_2-\vdots\,- \end{array}$$
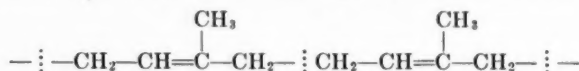
DR. THOMPSON (*communicated*): I am most interested in Harding's comments on polyisoprene, but cannot agree with his implied generalization that isoprene always polymerizes predominantly by 1,2-addition. We also have measured the spectra of some films of synthetic polyisoprene, and have found that some samples may actually predominate in the 1,4-addition, as suggested by the very strong band at 840 cm.$^{-1}$. Also, using the key bands which have already been mentioned for the other types of olefinic linkage, the spectra suggest that, in some polyisoprene samples at least, the 1,2-addition can occur in either of two ways, leading to structures of the type (I) and (II), in which the pendent groups are different. (I) is in the substituted isobutylene class, and (II) in the vinyl class.

$$\begin{array}{cc} \cdots-CH_2-CH-\cdots & \begin{array}{c}\mathrm{CH_3}\\|\end{array}\\ \begin{array}{c}|\\ \mathrm{C\cdot CH_3}\\ \|\\ \mathrm{CH_2}\\ \mathrm{(I)}\end{array} & \cdots-CH_2-C-\cdots\\ & \begin{array}{c}|\\ \mathrm{CH}\\ \|\\ \mathrm{CH_2}\\ \mathrm{(II)}\end{array} \end{array}$$
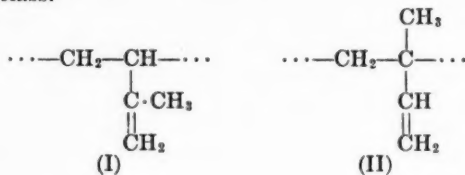
It is clear from all these results that particular conditions may favor the different methods of condensation, and we have here a good method for analyzing them.

DR. H. P. KOCH (*Welwyn*) said: Harding has observed marked dissimilarities in the spectra of rubber and gutta-percha, and some of these differences must be connected with the geometrical isomerism of the two polymers about the double bond of the repeating unit:

$$-CH_2-CMe{=}CH-CH_2-$$

To establish such a correlation we hope to have pure samples of the *cis*- and *trans*-isomers of dihydromyrcene available for infrared investigation shortly. Some progress would then be possible in the interpretation of those parts of the spectra associated with the internal molecular shape of the polymeric chains. It may be pointed out in this connection that the analogous pair of isomeric alcohols, geraniol and nerol, failed to reveal significant differences in their Raman spectra[5].

The difficulty of finding independent standards for checking or calibrating infrared absorption intensities of interpolymer spectra could be partly overcome by supplementation with data from ultraviolet spectroscopy which is a powerful analytical tool whenever conjugated or aromatic centers are present in the molecule. Many polymers can be made to give clear solutions in ultraviolet transparent solvents such as cyclohexane for this purpose. Thus, the proportion of styrene combined in Buna-S can be estimated by measuring the absorption band at 260 mμ, and it has been shown previously[6] how the mode of combination of Novalac resins with rubber could be determined by ultraviolet analysis.

DR. ALWYN G. EVANS (*Manchester*) said: The use of the infrared technique to determine whether monomer molecules link up on polymerization by the head-to-tail method or by the head-to-head method is interesting, especially for monomers of the 1,1-disubstituted ethylene type. For such monomers, *e.g.*, $CH_2{=}CX_1X_2$, the head-to-tail polymerization leading to the structure:

$$X_1 \quad X_2 \qquad X_1 \quad X_2 \qquad X_1 \quad X_2$$
$$\diagdown C \diagup \qquad \diagdown C \diagup \qquad \diagdown C \diagup$$
$$\diagup \qquad \diagdown C \diagup \qquad \diagdown C \diagup \qquad \diagdown$$
$$H_2 \qquad\qquad H_2 \qquad\qquad H_2$$
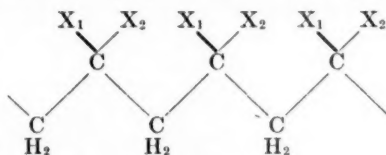
gives rise to the possibility of steric hindrance between the substituent groups X on one carbon atom and those on the next carbon but one. When the substituent groups X are CH_3, that is, when the monomer is isobutene, it is found that this steric interference between the methyl groups is quite large. A model of the polyisobutene molecule of the head-to-tail type can be built up only by successive rotation of the isobutene units with respect to each other, so that the methyl group of one isobutene unit fits in between the two methyl groups of the next isobutene unit. The structure so obtained is quite rigid, although the model carbon atoms used have a smaller van der Waals radius than the normal[1]. It is to this steric interference that the low heat of polymerization of isobutene has been attributed[7].

From the infrared examination of polyisobutene, Thompson and Torkington conclude that there may be a slight weakening of the carbon-carbon bonds, and this they attribute to the steric hindrance in the molecule.

The head-to-head, tail-to-tail, polymerization would lead to the structure:
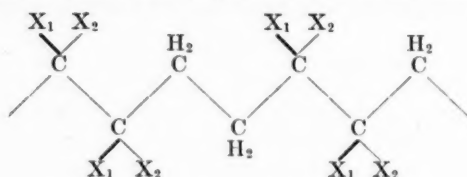
in which there is no possibility of steric interference between the substituent groups X. A model of the polyisobutene molecule of this structure shows the absence of steric hindrance. Rotation about the carbon-carbon bonds can occur in contrast to the rigid structure obtained for the head to tail model.

On polymerization the isobutene molecules join with each other by the head-to-tail method to give a polymer in which there is strong steric hindrance, and a consequent reduction of carbon-carbon bond strength. The fact that the alternative head-to-head, tail-to-tail method of polymerization, which would give an unstrained polymer molecule, does not occur, is of importance from the point of view of the mechanism of polymerization. By increasing the size of the groups X, the head-to-tail structure becomes more and more sterically unfavorable compared with the head-to-head, tail-to-tail structure. It would be interesting to see whether such an increase in the size of the groups X were accompanied by an increasing proportion of head-to-head addition, or whether, as in diisobutene, where X_1 is CH_3 and X_2 is $CH_2C(CH_3)_3$, polymerization is stopped altogether, and dimerization occurs[8].

DR. A. WASSERMANN (*London*) said: I should like to draw attention to the importance of spectroscopic measurements for entropy calculations, which in turn are of interest in connection with the mechanism of certain low or high molecular polymerizations. As an example, I refer to the reactions of butadiene. The first step in the high molecular polymerization leads to species of the formula C_8H_{12}. One such species can be represented by the straight chain diradical (A) referred to in Thompson and Torkington's paper. The formation of a bond between the first and sixth carbon atoms leads to 4-vinylcyclohexane (B) which, at about 600° Abs., is the product of the homogeneous gaseous dimerization of butadiene. It is of interest to find out whether (A) is an intermediate in the formation of (B) or whether the primary steps in the high molecular polymerization and in the dimerization are fundamentally different. To decide this question attempts have been made[8] to estimate the entropy change, ΔS, of the two processes 2 butadiene = (A) and 2 butadiene = (B). The quantity ΔS can be regarded as being the sum of three terms:

$$\Delta S = \Delta S_{rig.} + \Delta S_{vib. (\alpha)} + \Delta S_{vib. (\beta)}$$

where $\Delta S_{rig.}$ comprises the contributions of the various species supposed to be rigid, $\Delta S_{vib. (\alpha)}$ relates to relatively stiff vibrations of frequencies higher than 1000 cm.$^{-1}$ and $\Delta S_{vib. (\beta)}$ relates to the lower vibrations, or to torsional oscillations in the range 200 to 1000 cm.$^{-1}$ and to free or restricted internal rotations. The calculations[9] lead to the following result:

$$\left.\begin{array}{l} \Delta S/R = -\ 6 \pm 3 \text{ for species A} \\ \Delta S/R = -\ 12 \pm 5 \text{ for species B} \end{array}\right\} (T = 600°).$$

Both these figures are compatible with the experimental entropy change as

deduced from kinetic measurements; it follows, therefore, that this method of approach cannot be used to find out whether the formation of (B) is a side reaction of the low molecular link of a polymerization chain. The large inaccuracies are due mainly to the present incomplete knowledge of $\Delta S_{vib.}$ (β) but entropy calculations of the type here considered will doubtlessly lead to useful results if we know more about the vibrations and torsional oscillations down to 150 cm.$^{-1}$. It is improbable that, in benzene and in simple aromatic compounds, such low frequencies occur[10], but it is nevertheless possible that in other cyclic compounds some of the frequencies are very low[11]. The necessary information can probably be obtained by a combined investigation of the infrared and Raman spectra, by a determination of the band spacings in fluorescence and phosphorescence spectra and by measurements of the specific heats.

Mr. L. W. MARRISON (*Widnes*) (*communicated*): It would be interesting to know if the authors of this paper have been able to correlate the absorptions at 3.0, 5.8 and 9.75μ, observed in the spectrum of oxidized rubber, with any particular type of oxygen-containing structure. The possible analogy with the ketonic absorption at 1720 cm.$^{-1}$ observed by Thompson and Torkington in polythene seems to be very suggestive.

DR. SUTHERLAND (*Cambridge*) (*communicated*): The absorptions at 3.0 and 5.8μ occurring in oxidized rubber are due respectively to OH and C=O valency vibrations. These bands have been studied further by Harding and myself to see whether quantitative estimations of the OH and C=O bonds in oxidized rubber can be made by this means. Although rough estimates can be made fairly readily, accurate determinations (especially of the OH) present certain problems which have not yet been satisfactorily solved. The exact interpretation of the band at 9.75μ (which is much less well defined, since there are in fact several new overlapping bands due to oxidation in the region beyond 7.5μ) is not yet clear, but it is almost certainly to be associated with C—O bonds.

DR. THOMPSON said: With regard to some of the points made by Sutherland, I agree that the rules for differentiating classes of olefins must be used carefully with other than hydrocarbon molecules. Torkington has also found, for example, that in the allyl halides, as also with the vinyl halides[12], the frequencies of the bending oscillations of the C—H bonds shift according to the halogen atom which is attached, but rules are gradually being built up from which such shifts may be anticipated.

We, too, have found with samples of Nylon, other points of the kind mentioned by Sutherland, but not given in detail in our paper.

I was particularly interested in the work described by Sheppard and Sutherland on vulcanization, since Torkington and I have made some similar measurements in which the vulcanization by sulfur chloride was studied. The spectra of samples of crepe rubber which have been subjected to sulfur chloride vapor for varying times show marked differences, as shown in the diagram.

As vulcanization proceeds new bands appear, notably at 635, 680 and 895 cm.$^{-1}$, although there are other changes in the spectrum too. We should naturally try to correlate these new bands with the formation of C—S or S—S linkages, and to this end Trotter has been measuring the spectra of some alkyl disulfides, including the dimethyl, diethyl, dipropyl and dibenzyl derivatives, between 3-20μ. These alkyl disulfides have bands in the range 500-700 cm.$^{-1}$, but no very certain correlation can yet be made with the bands in the vulcanized rubber.

It is interesting also to note that, when vulcanization by sulfur chloride occurs, there is no marked change, in the early stages at least, in the absorption near 1600 cm.$^{-1}$ associated with the carbon-carbon double bonds, which agrees with the result found by Sheppard and Sutherland.

As regards the peculiar band at about 6.5μ associated by Sheppard and Sutherland with the stearate ion, we have found also that many sodium or potassium salts of fat acids, such as acetic, propionic, butryric, benzoic and oleic acid, have a band in the region 1530–1570 cm.$^{-1}$ (6.4–6.5μ), which agrees with their conclusion. The way in which the frequency associated with the carbonyl group varies in different compounds has been studied exhaustively by Trotter, and appear to lead to some very useful structural correlations which will be given later elsewhere.
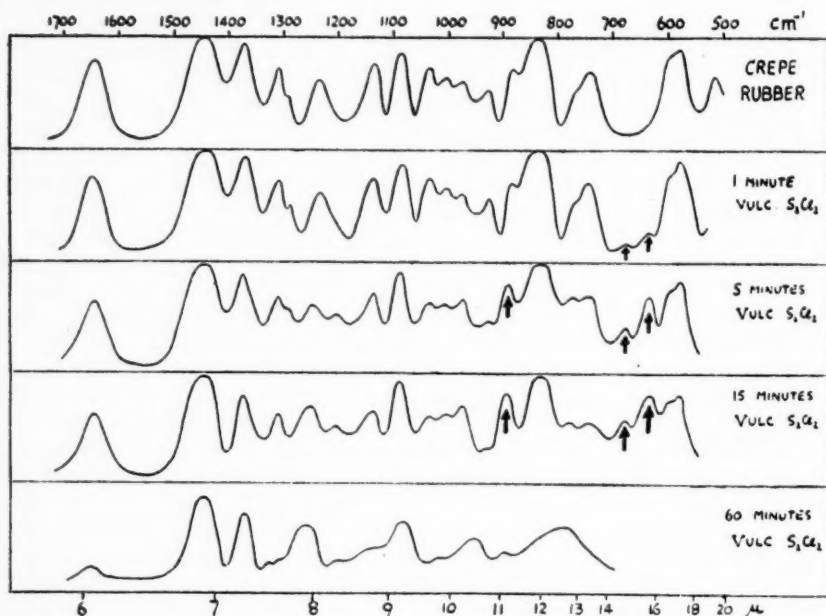
The points raised by Evans about polyisobutylene and polyvinylidene chloride are interesting. I agree with him that what is required is a systematic study of how the various modes of condensation of olefinic compounds are related to the chemical and physical nature of the other radicals present, such as halogen, cyano or alkyl groups. We hope shortly to undertake a planned investigation of this kind.

With regard to the other questions raised, the changes brought about in the oxidation of polythene can be very well explored by infrared absorption, and have given interesting results.

MR. SHEPPARD (*Cambridge*) said, in introducing his paper with Sutherland: We should like to add the following points:

(1) The classification of C—H bond strengths by Linnett[13] makes it unlikely that the "lone" hydrogen atom attached to the double bond in rubber could give rise to a ν C—H absorption band at as low a wave length as 3.1μ,

and hence it would seem more likely that this is a weak combination frequency. An alternative explanation is that rubber contains a small number of $C \equiv C$ triple bonds, and that it is hydrogen atoms attached to these which give rise to the absorption band at 3.1μ. In agreement with this the band at approximately 5.0μ could be interpreted as the valency vibration of such triple bonds. We are now also of the opinion that the possibility of this band being due to the hydroxyl absorption cannot be excluded.

(2) Further work has been carried out on accelerated mixes of the type A4 containing larger amounts of sulfur and accelerator with the object of detecting any new bands other than those found in cured mix A1, *i.e.*, of detecting any bands which can be directly related to changes in the nature of the product brought about by the use of accelerators. No such bands have been discovered, and it would seem that the use of this type of organic accelerator (mercaptobenzothiazole type) gives rise to the same final changes in the rubber molecule as does straight sulfur vulcanization. Another result in support of this view is that the intensity of the 10.4μ band in a wide series of vulcanizates is clearly related to the amount of sulfur incorporated. Similar quantitative work is now in progress on the 17.0μ band, and on the extension of these spectra to 30μ.

(3) In many cases, especially when "ultraaccelerators" are used, good properties of the vulcanizate can be obtained with the incorporation of much smaller amounts of sulfur than we have discussed. This suggests the possibility that some of the changes which we have observed in the spectrum on vulcanization may not be directly related to the important physical properties by which we characterize a vulcanized rubber, but are to be correlated with secondary physical effects. Work is now in progress on mixes in which the optimum vulcanization properties are obtained with the minimum amounts of vulcanizing agents.

Mr. J. HARVEY (*London*) (*communicated*): It is interesting to note, from the work described in the paper of Thompson and Torkington, the introduction of a new weapon in the attack on the structure of natural and synthetic polymers, and from the evidence presented it is clear that we may expect in the near future to know very much more than we know at present of the chemical configuration of these materials.

Three points may be raised for further comment. First, in connection with the degree of polymerization of these materials, it is stated that no significant differences have been noted in the spectra of samples of polyisobutylene of different molecular weight. It is to be expected that, for polymers such as polyvinyl chloride or polystyrene, a band or bands due to end-groups should be observable, the intensity of which would give some measure of the degree of polymerization. Moreover, the assignment of bands to end-groups might lead to an advancement of knowledge of these groups, about which little information is available in many cases at the present time. Polyisobutylene, it is felt, is not a good example, for if the chain termination is a methyl group, as is possible, the effect suggested will probably not be observable.

Secondly, the section dealing with head-to-head or head-to-tail configurations is noted; it will be interesting in due course to know how far the results of the present investigations bear out the configurations put forward by Marvel and his coworkers[14] on the results of a chemical examination.

Finally, it is to be hoped that workers in this field will soon have an opportunity to include in their studies an examination of the so-called mixtures of polymers and plasticizers. The suggestion has been put forward[15] that, in some

cases, notably with polymers derived from monomers of the type $CH_2=CHR$, the interaction which takes place may include the formation of bonds of a weak chemical nature. Hydrogen bonds are envisaged between the active groups (carboxyl groups in the case of esters such as phthalates) of the plasticizer molecule and the carbon atoms, to which the substituents are attached, in the polymer chain.

It is thought that a comparison of the absorption spectra of the separate components with those of mixtures of polymer and plasticizer may give confirmation to this hypothesis. In this study, an examination of the C—H stretching vibrations at about 3μ may be of use, and it is perhaps unfortunate that in only four of the spectra of vinyl-type polymers recorded, does the scale extend down to this wave length.

DR. L. KELLNER (*London*) (*communicated*): Thompson and Torkington raise the question whether an estimate of the length of the chain can be formed from the spectra produced by compounds of varying chain length. At the present stage of theoretical treatment, there does not seem much hope that this question can be solved. I have shown in my contribution, "The C—C valency vibrations of organic molecules", that the C—C— valency vibrations of a normal chain lie between 809 and 1143 cm.$^{-1}$, whatever the length of the chain. The number of frequencies within these limits increases with the number of links. The bands, therefore, crowd closer and closer together, but it is practically impossible to resolve the bands in the case of molecules of high molecular weight. On the other hand, it may not be impossible to estimate the length of a chain from the intensity of the complex band between 809 and 1143 cm.$^{-1}$. For that purpose, it would be necessary to make an experimental investigation of the influence of the number of linkages on the intensity of the corresponding bands and to calculate the total absorption between 809 and 1143 cm.$^{-1}$ for every molecule under investigation. In the case of compounds containing side chains involving C—C, C—N and C—O bonds, the side chains form an integral part of the whole molecule where the vibrations are concerned. The spectrum corresponds then to that of an isomer of the normal chain with the side chains occurring at regular intervals. The case of C=O, C—H, C—Cl, etc., groups in the side chains is, of course, different since their oscillations are practically independent of the C—C frequencies of the main chain.

DR. SUTHERLAND (*Cambridge*) (*communicated*): There are two points which Sheppard and I should like to make with reference to the absorption spectra given by Torkington and Thompson for rubber vulcanized by sulfur chloride. Among the changes in the spectra which were not specifically listed by them we note that a band near 10.4μ gradually increases in intensity during vulcanization. This is where we found the most marked change in the spectrum with straight sulfur vulcanization. It suggests that these two methods produce some common structural change in rubber. The second point is that since vulcanization by sulfur chloride involves the chemical incorporation of chlorine as well as sulfur into the rubber, it is to be expected that some of the new bands may involve Cl linkages which are not essentially related to vulcanization.

MR. TORKINGTON and DR. THOMPSON (*communicated*): We agree with (Mrs.) Kellner that the changes in the spectrum of a long-chain paraffin as the number of carbon atoms increases are very small, and give little hope of a direct determination of the chain length from the magnitudes of special types of chain frequency. We also agree with her that the mathematical treatment of such systems as vibrating groups of atoms is not yet far advanced, or as precise

as one might wish. We do not agree, however, with the approximations in the model which she would suggest for some of the molecules in attempting to compute the vibration frequencies, since it is not possible to separate the carbon-carbon oscillations from other vibrations to the extent which she suggests. As already stated in this discussion, with (Miss) Simpson and Sutherland, a more exact treatment is possible for hydrocarbon molecules, and (Mrs.) Kellner's speculations about the strengthening of a band in the region of 1000 cm.$^{-1}$ in the case of long chain paraffins are not confirmed by the facts.

The determination of chain lengths by other, less direct, methods, in which, for example, the estimation of end groups may be important, is being carefully explored.

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VULCANIZATION OF RUBBER WITH
SYNTHETIC RESINS *

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INTRODUCTION

Since Goodyear's invention the vulcanization of rubber has been the subject of thorough technological, physical and chemical investigations.   As a result of this work, carried out all over the world, we now have some idea of what actually may happen when a complicated substance like rubber is heated with sulfur.   Besides the possibility of "physical" changes in the rubber network, most rubber chemists are now inclined to believe that the typical transformation of the plastic to the elastic state is caused by the formation of a relatively small number of interlinkages between the rubber molecules, which may be wholly or partly the result of chemical combination of rubber and sulfur.

Theoretically it is improbable that sulfur or sulfur-containing compounds are the only agents by means of which rubber can be vulcanized.   Innumerable substances were therefore mixed and heated with rubber, but it was not until 1915 that Ostromislensky[1] discovered the possibility of vulcanizing rubber with polynitrobenzenes and with benzoyl peroxide.

Since then several other vulcanizing agents have been found[2], so that up to about 1939 the following groups[2] can be designated

1. Sulfur and sulfur compounds
2. Polynitrobenzenes and polynitronaphthalene
3. Benzoyl peroxide
4. Diazoaminobenzene and derivatives
5. Quinones and halogenated quinones
6. Quinone mono- and diimines
7. Quinone mono- and bis-haloimines
8. Quinone mono- and dioximes.
9. Grignard reagents and zinc alkyls
10. Azochloride (N-N'-dichloroazodicarbonamidine)
11. Inorganic agents[3]: mercuric oxide, lead dioxide, among others.

Fisher also adds a group of compounds which, though having no vulcanizing properties by themselves, can vulcanize rubber when used in combination with an oxidizing agent.   This group comprises hydroquinone, phenol, cresol, thiols, p-hydroxydiphenylamine and others, as well as aromatic amines.

Some care must be taken in using the term "vulcanized"[4].   The author bases the terms "vulcanization" and "vulcanized" on the state of the material only, but never on the actual heating of the rubber with sulfur or some other agent. A practical definition[5], which also holds for nonsulfur vulcanizing agents, is

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that "vulcanization is the process by means of which a rubber or rubberlike material is irreversibly transformed from the preponderantly plastic state into the preponderantly elastic, nonplastic state".

In this article, the term "vulcanization" will be used in this sense. Considering this definition, it is doubtful whether all the substances given by Fisher[2] really are vulcanizing agents, because he calls rubber vulcanized as soon as the material no longer dissolves in benzene, which is a far less sharp criterion. Insolubility is reached much earlier than elasticity, as it is possible to obtain insolubility with still quite plastic samples.

The definition of "vulcanization" given may be completed by a specification of the term "preponderantly elastic", which can easily be furnished by giving, for example, a maximum value for the permanent set at a certain temperature and initial elongation. It is realized that such definitions have more practical than theoretical value, nevertheless it is possible that a more theoretical description can be reached starting from this point.

Though many substitutes have been found, sulfur[5] remains the vulcanizing agent par excellence, because only with sulfur can the maximum properties of the vulcanizate be reached. Vulcanization with other agents, for instance, benzoyl peroxide or m-dinitrobenzene, gives products which are not used in practice. Besides having as a rule far poorer mechanical properties than sulfur vulcanizates, nonsulfur vulcanizates are often unstable, in consequence of which they age too rapidly to be of practical use.

THE CHEMICAL COMBINATION OF RUBBER AND SYNTHETIC RESIN

A considerable number of patents are claimed for the combination of rubber and synthetic resins. Generally, the following groups can be distinguished:

a. The addition of rubber to synthetic resins, to obtain moulded products with a certain elasticity. This appears to be used in a few cases. Up to 5 per cent rubber is added. The products are hard, but less brittle.

b. The addition of powder of hardened synthetic resin to a rubber mixture as a filler. As this has not shown any advantage over the use of the much cheaper inorganic fillers, the practical use is limited.

c. The addition of nonhardened, thermosetting moulding powder to a rubber-sulfur mixture with the intention of combining the hardening of the resin with the vulcanization of the rubber. This is used in special cases. The products are hard and do not show high elasticity.

d. The addition of nonhardened, thermosetting moulding powder to a rubber-sulfur mixture, with the intention not only of combining the hardening of the resin with the vulcanization of the rubber, but also of obtaining a chemical combination of resin and rubber. Though it is difficult to prove this combination, it is claimed in some cases. It is unlikely that there is an essential difference between d and c, because also in those cases, where chemical combination is claimed, only hard products are obtained.

e. The heating of rubber—vulcanized or unvulcanized—or other polymeric substances, with compatible resins, usually with the intention of forming raw material for laquers and varnishes[6].

The hardening of a resin is a process which usually has a much higher reaction rate than the possible combination of rubber and resin. The reaction between rubber and normal sulfur-vulcanizing agents (combination sulfur-accelerator) is also much quicker. As long as these agents are present, and as long as relatively quickly hardening resins are used, there is little chance that

rubber and resin will combine chemically. On the other hand, the combination of rubber and resin will be successful only when a chemical combination between rubber and resin is achieved, since many practical experiments have proved that pure mixtures are without much significance.

Thus the principles on which the investigations were started were the following:

(1) to try to combine rubber and resin only, in the absence of any vulcanizing agent;

(2) to use slow-hardening resins;

(3) to try to obtain rubber and resin in one phase.

As a result it was found that vulcanized rubber practically equivalent to technical rubber-sulfur vulcanizates can be obtained by mixing and heating rubber with certain synthetic resins. It can be proved that the rubber and resin are chemically combined.

SYNTHETIC RESIN AS SOLE VULCANIZING AGENT

The three principles given in the preceding paragraph exclude a large part of the synthetic resins. Most of the normal moulding powders are not compatible with rubber, so there is little chance that a combination will take place. Moreover, when we consider the phenol-formaldehyde moulding powders, as a rule a three-dimensional structure is built up with relatively high speed; the reaction resin-resin is preferred, and a reaction rubber-resin does not take place.

In the group of the phenol-formaldehyde resins, compatibility with rubber can be obtained by starting from substituted phenols. A lower reaction rate is obtained ty taking phenols with only two reaction-favorable positions in the molecule, so that three-dimensional structures are impossible. A resin of this type is Albertol 142-R[7], which in fact has excellent vulcanizing properties. Of course there are other resins obtainable which can do the same, but the compositions of these resins are often unknown, so it is not certain whether they belong to the same class. Apart from Albertol 142-R, rubber can also be vulcanized with Durophen 219-W[7], with Bakelite resin BR-3360[8], and some others.

Compatibility with rubber and a low reaction rate are not enough to ensure a vulcanizing reaction with rubber. A resin like R-254[8], though closely resembling BR-3360, is absolutely negative.

A considerable number of resins have been tested for their activity toward rubber, most with negative results. It is not possible to predict with certainty whether or not a resin will vulcanize. Compatibility and a low reaction rate do not run parallel with rubber-vulcanizing properties[9]. When the configuration of the resin or vulcanizing compound is precisely known, a prediction may be possible, but with many resins—and certainly with resins which can be bought on the market—this is not the case.

The simplest method of determining whether or not a resin vulcanizes is to try it. Though this may be done in different ways, a standard method has been developed for this purpose, viz., to mix 100 parts (by weight) of rubber with 40 of resin and heat 2 hours in a press between parallel plates at 155° C. If no reaction takes place, the mixture disintegrates on opening the press, and only a sticky mass is obtained, which is wholly or partly soluble in benzene. In some cases the resin hardens, while the rubber depolymerizes under the influence of heat. Then a slab may be formed, but it is hard and sticky, and disintegrates in benzene.

When the resin has vulcanizing properties, however, an elastic slab is obtained, which loosens from the mould without difficulty and keeps its shape on swelling in benzene. Such a mixture can be vulcanized and the properties of the vulcanizate can be determined in the same way as with ordinary rubber-sulfur mixtures.

This method is simple and certain; a resin which, when tested in this way, does not obviously give a vulcanizate must be considered negative towards rubber, since neither longer nor higher heating, nor using more resin, gives any other result.

The optimum amount of most resins is about 40 parts (by weight) to 100 of rubber. This seems much more than is necessary for sulfur vulcanization, but considering the big difference in molecular weight, it is less. We must compare the rubber-resin vulcanization with rubber-sulfur vulcanization without accelerators. Then to 100 of rubber 8 of sulfur are necessary, that is, to 68 g (1 unit C_5H_8) of rubber 0.17 mole of sulfur. When we consider a vulcanizing resin derived from a substituted phenol, for example pentaphene (p–t-amylphenol), then the lowest molecular weight possible is that of the dialcohol, 1,2,6,4-$HO(HOCH_2)_2C_6H_2CEtMe_2$, molecular weight 224. 40 of resin to 100 of rubber is then equivalent to 0.12 mole per unit rubber, against 0.17 mole for sulfur. For this comparison we must suppose that one molecule of sulfur, like one molecule of resin, is able to interlink two points of the rubber thread molecules.

The normal vulcanization temperature for rubber-resin mixtures is at 150–160° C; most experiments were carried out at 155° C. This is somewhat higher than with rubber-sulfur mixtures, where the temperature of 147° C is usual. The vulcanization time varies from 30 to 120 minutes; as there is no sharp optimum, a time of two hours is usually taken to be sure of a good cure. Considering the fact that for the 100 rubber 8 sulfur mixture optimum vulcanization lies at 2–3 hours at 147° C, it is clear that the reaction rate of the rubber-resin vulcanization is of the same order of magnitude as the reaction rate of the rubber-sulfur vulcanization.

Rapid and ultrarapid vulcanization, as with sulfur-accelerator combinations, has not been observed for resin vulcanization, and is not likely to be observed, as the resin molecules are always much less mobile than the sulfur molecules.

SYNTHESIS OF VULCANIZING RESINS

In the course of the investigations described, many resins and other compounds with rubber-vulcanizing properties were synthesized, of which only the vulcanizing resins from pentaphene (p–t-amylphenol) and formaldehyde are treated in this paper.

One mole of pentaphene, 2 moles of formaldehyde and 0.2 mole of NaOH[10] are mixed with water and heated for 30 hours at 50° C. A resin and a water layer are formed. The NaOH is neutralized with hydrochloric acid, and the resin is washed with water. To remove the last traces of water the resin is heated at 50° C *in vacuo*. A clear brownish yellow syrup is obtained.

When 40 parts of this resin are mixed into 100 parts of rubber on an ordinary mill, and the mixture is heated in a press for two hours at 155° C, a perfectly elastic vulcanizate is obtained, which loosens easily from the mould. The mechanical properties of these vulcanizates are low, but, as with sulfur vulcanizates, the permanent set is close to zero, which proves complete vulcanization. In benzene, the vulcanizate only swells, but keeps its shape, while the unvulcanized mixture of course rapidly dissolves.

To test the influence of the condensation time on the properties of the vulcanizates, three more resins from pentaphene and formaldehyde have been synthesized. One mole of pentaphene, 2 moles of formaldehyde and 0.2 mole of ammonia were mixed with water and heated at 50° C for 15, 30 and 60 hours. By heating *in vacuo* after separation from the water layer, the resins may easily be neutralized and dried. The three resins which were formed in this way are syrups with increasing viscosity. All three have vulcanizing properties, though there are marked differences in their reaction rates. The resin with the longest condensation time gives the best results. The number of possibilities of interlinking with rubber certainly goes through a maximum with increasing condensation time, so this maximum has not been passed in 60 hours.

When rubber is heated for two hours at 155° C with pentaphene alone, no reaction takes place. Reaction of phenols with rubber have been described, but strong "catalysts", *e.g.*, a large amount of sulfuric acid, are always added. The rubber disintegrates and resinlike products are formed.

PROPERTIES OF RUBBER-RESIN VULCANIZATES

Though slight alterations are sometimes required, in general the usual technique for rubber-sulfur mixtures can be retained for the rubber-resin vulcanization. Some resins give very sticky mixtures, but this difficulty can be met by cooling the rolls to 30–40° C. On the other hand, with many resins mixtures are obtained which can hardly be distinguished from normal technical sulfur mixtures.

In all cases calendering is possible without any difficulty providing the right temperatures are maintained. Before forming an article it is advisable to cool the mixture to 20–25° C in most cases. Sometimes the vulcanized article sticks to the mould, but matters usually take the same course as with sulfur vulcanizates.

(a) *Vulcanizates of rubber and resin, with exclusion of any other vulcanizing agent or filler.*—Following the standard method for testing resins for vulcanizing properties, a mixture of 100 parts of rubber and 40 of resin is heated for 120 minutes at 155° C. For many resins these conditions are also the optimum ones; for many others, however, the quantity of resin and the vulcanization time and temperature may differ considerably from these norms.

Complete vulcanization is possible with 10 parts of resin to 100 parts of rubber, while with 40 of resin the optimum may be reached in 30 minutes at 155° C instead of two hours. The mechanical properties are also very dependent on the quantity and kind of resin. This is demonstrated by the data of Table 1.

The low permanent set of the rubber-resin vulcanizates, which runs parallel with high elasticity, proves that vulcanization is complete. Hardness and modulus depend in the first place on the quantity of resin, though the kind of resin may also be of importance. The reason for the large difference in tensile strength is not clear, but may be connected with the interlinking possibilities of the resin itself.

A high elongation and a low modulus, as with the 100 rubber 8 sulfur mixture, the data of which are also given in Table 1, is not probable for mixtures of 100 rubber and 40 resin, as the resin molecules probably remain much shorter than the rubber molecules. The difference between the 100 rubber 8 sulfur and the 100 rubber 10 Bakelite resin mixtures is probably caused by a lower number of rubber-interlinking spots in the rubber-resin mixture, the number of

TABLE 1

VULCANIZATION OF NATURAL RUBBER WITH SYNTHETIC RESINS

Rubber		100	100	100	For comparison:
Albertol 142-R		50	—	—	100 rubber
Bakelite-resin 3360		—	10	40	8 sulfur
Vulcanization temperature (° C)		155	155	155	147
Vulcanization time (minutes)		120	120	30	180
Method			normal Schopper rings		
Tensile strength	kg. per sq. cm.	25	57	111	162
Elongation at break	percentage	230	634	571	940
Modulus at 100%	kg. per sq. cm.	9	3	6	4
Modulus at 200%	kg. per sq. cm.	21	4	13	5
Modulus at 400%	kg. per sq. cm.	—	12	48	11
Hardness	Shore Durometer A units	49	30	40	31
Elasticity	Shore Elasticity units	79	86	88	89
Permanent set[11]	percentage	2[12]	4	2	5

moles of vulcanizing agent per unit of rubber being 0.17 for the sulfur, and below 0.03 for the resin mixture.

(b) *Influence of catalysts.*—When we compare the vulcanization and the properties of the vulcanizates of the 100 rubber 8 sulfur mixtures with those of modern mixtures with low percentages of sulfur, *e.g.*, 1 per cent, and ultrarapid accelerators, the principal difference lies in the vulcanization time and in durability of the products[12]. The tensile strength is also higher when sulfur-accelerator mixtures are used.

With rubber-resin vulcanizates, matters are somewhat different. In contrast to the case of rubber-sulfur vulcanizates, the aging is excellent. But the tensile strength is lower (compare Table 1), and it is desirable to cut down the vulcanization time.

Several substances have been investigated for their value as a catalyst, but in most cases the result was negative. Adding sulfur caused a less intense rubber-resin reaction, as sulfur prevents the resin from interlinking the rubber by reacting itself. Normal rubber-sulfur accelerators are without effect. Some acceleration of the rubber-resin is possible with chloranil and with lead peroxide, which, however, are both vulcanizing agents themselves, though weak ones[13].

A strongly negative influence is shown by hexamethylenetetramine. A mixture of 100 rubber and 50 Albertol 142 R vulcanizes in 120 minutes at 155° C. A mixture of 100 rubber, 50 Albertol 142-R and 5 hexa shows no trace of vulcanization: on heating only a plastic syrup is obtained. With most resins the same effect has been found; only with Bakelite Resin 3360 does the vulcanization power remain, though lessened. The effect may be caused by a further condensation of the resin under the influence of hexa before a chemical bond with rubber is formed. This phenomenon should then be analogous to the effect of sulfur, which limits the mobility of the rubber and so prevents a reaction with the resin.

An important increase of the tensile strength, though no shortening of the vulcanization time, is caused by magnesium oxide. Even the addition of as

little as 3 per cent to rubber may cause the tensile strength to rise by 200 per cent. A typical example is given in Table 2 and in Figure 1.

TABLE 2

EFFECT OF MAGNESIUM OXIDE ON RUBBER-RESIN VULCANIZATION

Rubber		100	100	100	100	100	100	100
Albertol 142-R		50	50	50	50	50	—	—
Bakelite resin 3360		—	—	—	—	—	40	40
Magnesium oxide		—	3	5	20	100	—	1
Vulcanization temperature (° C)		155	155	155	155	155	155	155
Vulcanization time (min.)		120	120	120	120	120	30	30
Method				normal Schopper rings				
Tensile strength	kg. per sq. cm.	25	77	96	181	167	111	162
Elongation at break	percentage	230	462	546	610	548	571	587
Modulus at 100%	kg. per sq. cm.	9	13	10	16	23	6	8
Modulus at 200%	kg. per sq. cm.	21	25	19	30	41	13	19
Modulus at 400%	kg. per sq. cm.	—	58	49	74	105	48	67
Hardness	Shore A	49	57	58	60	77	40	45
Elasticity	Shore	79	82	85	79	50	88	88
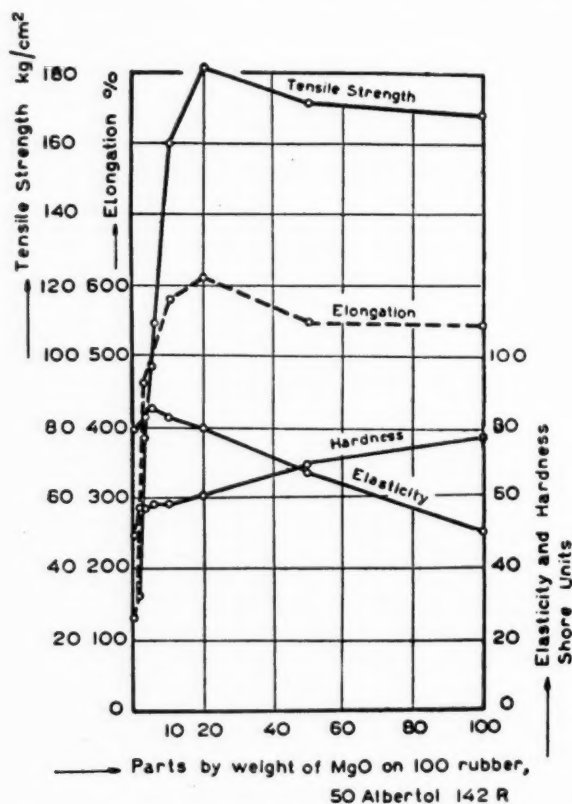
FIG. 1.—Effect of magnesium oxide on rubber-resin vulcanization.

Contrary to normal reinforcing fillers, such as carbon black, magnesium oxide also has a pronounced effect when added in very small quantities. The sharp rise of the tensile strength curve must be due to some other effect than reinforcement alone. Magnesium oxide may, therefore, be called a catalyst for the rubber-resin reaction. It does not act in the same way with all the resins tested, but up to now no vulcanizing resin has been found with which magnesium oxide has no effect at all.

Fisher[14] describes the vulcanizing effect of the combination of substances like hydroquinone, phenol and others with an oxidizing agent like lead peroxide. As rubber can be vulcanized with quinone alone, it is clear that hydroquinone plus peroxide, giving quinone, can do the same. With phenol the reaction is less simple, but the phenol may be oxidized and the rubber may also be vulcanized by the lead peroxide. The situation with vulcanizing resins plus magnesium oxide is quite different, for in the first place the resin also vulcanizes without the magnesium oxide; in the second place magnesium oxide is not an oxidizing agent, and in the third place vulcanization of rubber with magnesium oxide alone is impossible.

(c) *Influence of fillers.*—Much as with synthetic rubbers, only with an active filler such as carbon black can the tensile strength reach the same level as with normal natural rubber-sulfur vulcanization. An example of the influence of carbon black is given in Table 3 and in Figure 2.

TABLE 3

INFLUENCE OF CARBON BLACK ON RUBBER-RESIN VULCANIZATES

Rubber		100	100	100	100	100	100
Albertol 142-R		50	50	30	30	30	30
Magnesium oxide		—	—	5	5	5	5
Carbon black		—	30	—	15	25	45
Vulcanization temperature (° C)		155	155	155	155	155	155
Vulcanization time (min.)		120	120	120	120	120	120
Method				normal Schopper rings			
Tensile strength	kg. per sq. cm.	25	95	130	170	206	223
Elongation at break	percentage	230	306	624	579	572	485
Modulus at 100%	kg. per sq. cm.	9	24	7	11	17	30
Modulus at 200%	kg. per sq. cm.	21	56	13	23	31	60
Modulus at 400%	kg. per sq. cm.	—	—	38	69	94	168
Hardness	Shore A	49	72	48	60	68	84
Elasticity	Shore	79	65	90	85	75	58
Permanent set	percentage	—	—	3	10	14	23

When no magnesium oxide is present, the effect of carbon black shows a maximum, which lies much lower than is the case with rubber-sulfur vulcanizates. 5 parts of magnesium oxide have a greater effect than 30 parts of carbon black; the combination of magnesium oxide and carbon black gives a tensile strength of more than 200 kg. per sq. cm. Yet the permanent set is higher and the recovery is slower than is the case with sulfur vulcanizates.

Zinc oxide has no special effect, but behaves like an inert filler.

(d) *Summary of properties.*—The best results are obtained by combining rubber, resin and a little magnesium oxide. Carbon black can be added when a high tensile strength is required. For aging tests an antioxidant is added, but more ingredients are not necessary.
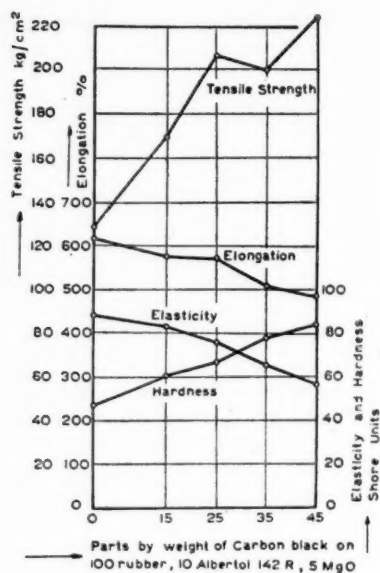
FIG. 2.—Influence of carbon black on rubber-resin vulcanizates.

Table 4 gives the properties of several typical rubber-resin vulcanizates.

TABLE 4

PROPERTIES OF TYPICAL RUBBER-RESIN VULCANIZATES

							For comparison: mean values of normal rubber-sulfur-accelerator vulcanizates	
Rubber		100	100	100	100	100		
Albertol 142-R		30	30	50	50	—		
Bakelite resin 3360		—	—	—	—	40		
Magnesium oxide		5	5	—	10	10		
Carbon black		—	45	30	10	—		
Aldol-α-naphthylamine		1	1	—	—	—		
Phenyl-β-naphthylamine		—	—	—	—	2	without fillers	with carbon black
Vulcanization temperature (° C)		155	155	155	155	155	147	147
Vulcanization time (min.)		60	60	120	120	60	20	20
Method				normal Schopper rings				
Mechanical properties								
Tensile strength	kg. per sq. cm.	112	220	95	160	92	225	225
Elongation at break	percentage	660	553	306	495	570	750	600
Modulus at 100%	kg. per sq. cm.	5	25	24	23	4	6	17
Modulus at 200%	kg. per sq. cm.	8	48	56	45	9	11	37
Modulus at 400%	kg. per sq. cm.	28	132	—	108	44	28	115
Hardness	Shore A	40	78	72	66	40	42	64
Elasticity	Shore	91	65	65	75	75	92	71
Permanent set	percentage	7	21	—	18	14	4	10
Abrasion (Grasselli)	cu. mm. per kg.	0.6	0.4	—	—	—	1.4	1.4
Aging								
Decrease after ⎤ tens. strength	percentage	3	13	—	0	0	0	0
two weeks in ⎬ elongation	percentage	2	7	—	0	1	15	15
air at 70° C ⎦								
Time of 25% ⎤ in tens. str.	weeks	7	5	—	8	4	8	8
decrease in ⎬ in elongation	weeks	22	10	—	>8	32	7	6
air at 70° C ⎦								
Swelling in organic solvents								
Swelling after ⎤ in benzene	percentage	—	—	253	333	—	325	300
1 week at ⎬ in naphtha	percentage	—	—	175	266	—	300	275
20° C ⎦								

The Schopper curves from series of the same composition as the first two mixtures of Table IV are given in Figures 3 and 4 as a function of the vulcanization time.

From these figures it may be seen that the influence of prolonged heating is only slight. This is in accordance with the data of Table 4 and the curves of
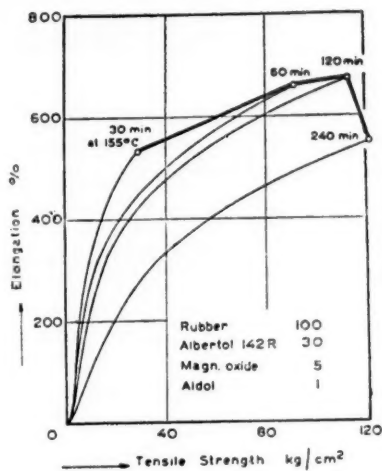
FIG. 3.—Schopper curves from rubber-resin vulcanizates without fillers.
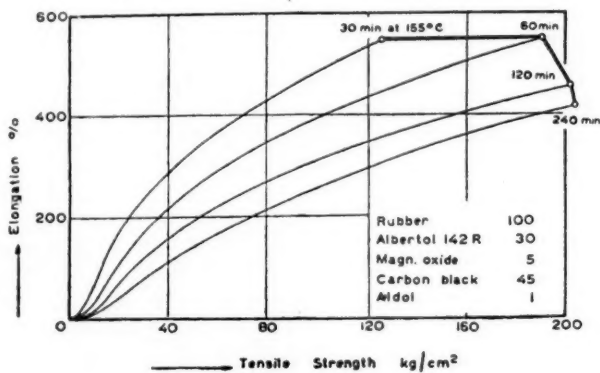
FIG. 4.—Schopper curves from rubber-resin vulcanizates with carbon black.

Figure 5; aging of the rubber-resin vulcanizates is at least as good as the aging of low-sulfur vulcanizates.

Rubber-resin vulcanizates seem to have a low abrasion, but it must be kept in mind that abrasion measurements are not very exact and that it is difficult to obtain a trustworthy comparison between different kinds of vulcanizates.

The swelling in organic solvents is of the same order of magnitude as is the swelling of sulfur vulcanizates. When, however, carbon black is added and

magnesium oxide omitted, the swelling in benzene as well as in naphtha is lower than is the case with sulfur vulcanizates, though these resin vulcanizates also have lower mechanical properties.
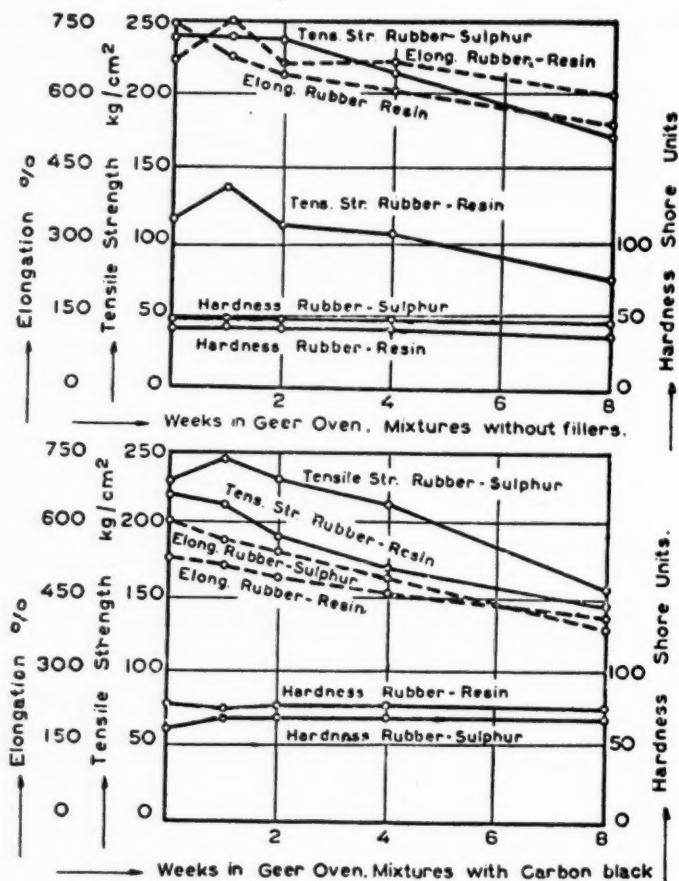
FIG. 5.—Aging of Geer-oven rubber-resin vulcanizates.

VULCANIZATION OF BALATA, GUTTA-PERCHA AND SYNTHETIC RUBBER WITH SYNTHETIC RESIN

Balata and gutta-percha both give a reaction with sulfur and form a "vulcanizate"[15]. The principal difference between the "vulcanizate" and the raw material lies in the widening of the region of elasticity more than in a difference in the mechanical properties. Moreover, at room temperature the reaction products as well as the raw material are crystallized, so that, when a comparison is made at this temperature, an essential change in the mechanical properties, as is the case with rubber, cannot be expected. The most striking feature is a decrease of the yield value, which is greater for gutta-percha than for balata.

Using the term "vulcanization" as the definition already given, neither

balata nor gutta-percha can be vulcanized with sulfur, since it is not possible to obtain a preponderantly elastic state (at room temperature).

Preliminary tests have shown that both balata and gutta-percha can react with resin. With balata the effect is most evident, as a product is formed which is elastic at room temperature, and therefore differs widely from the raw material. Here the term vulcanization, meaning the transformation from the plastic into the elastic state, is correct.

With gutta-percha the effect of "vulcanization" with a resin resembles that with sulfur. At 20° C the products are all crystallized, so that only at higher temperatures is elasticity present.

The synthetic rubbers derived from butadiene and derivatives can be vulcanized with synthetic resin in the same way as natural rubber. Rubbers like Perbunan and Buna-S can be vulcanized with resins like Albertol 142-R and Bakelite Resin 3360. A mixture of 100 Perbunan and 50 Albertol 142-R gives, on heating at 155° C for two hours, a vulcanizate with a tensile strength of 93 kg. per sq. cm., an elongation at break of 447 per cent, and an elasticity (Shore) of 80. With Buna-S and Durophen 219-W these values are 58, 631 and 70. As far as vulcanization with resins is concerned, there seems to be no fundamental difference between natural and synthetic rubbers.

CONFIGURATION OF RUBBER–RESIN VULCANIZATES

The first question which must be answered concerning the configuration of the rubber-resin vulcanizates is whether or not rubber and resin are chemically combined. In this particular case, dealing with a system of two high polymers, the molecules of rubber and resin may be entangled in such a way that plastic flow is impossible. and the material becomes elastic without any chemical bond being formed. The technological investigations of the vulcanizates, however, are not in accordance with this hypothesis, for the permanent set is as low as is the case with a good grade of sulfur-vulcanized rubber; hence formation of primary bonds between rubber and resin molecules is probable. Moreover, with 10 parts of resin a good vulcanizate with a low permanent set may be formed (see Table 1); if the vulcanizing effect were caused by entanglement alone, 10 parts of resin to 100 parts of rubber certainly would not be enough.

A more direct method is followed to prove chemical bonds between rubber and resin by extracting the vulcanizates with acetone and with benzene, and by comparing natural rubber with the analogous, but saturated and therefore inert high polymer Oppanol B-200 (polyisobutene).

Mixtures of 100 rubber or 100 Oppanol B-200 with 40 Bakelite Resin 3360 were prepared and heated for two hours at 155° C. With rubber a vulcanizate is formed, while the Oppanol-resin mixture appears to be much the same before and after the heating; elastic, but with a tendency to cold flow.

These two products were finely divided and extracted in an ordinary Soxhlet apparatus with acetone[16]. The results are given in Figure 6; the data are corrected for 3 per cent natural resin in the rubber.

As can be seen from Figure 6, the principal difference lies in the slope of the curves. The rubber-resin vulcanizate gives a practically constant value after a few hours, while with the Oppanol-resin mixture no equilibrium is reached. Nevertheless it takes a long time to extract the resin from the Oppanol, which may be due to an entanglement of the two systems.

Figure 7 gives an unequivocal answer to the question whether chemical combination takes place or not. The benzene extract of the (acetone-extracted)

rubber-resin vulcanizate is practically zero, while the heated Oppanol-resin mixture rapidly dissolves in benzene.

The resin alone, before and after heating for two hours at 155° C, is soluble in acetone as well as in benzene.   Oppanol and (unvulcanized) rubber are both soluble in benzene but not in acetone.

Thus rubber and resin, when heated separately, remain soluble in benzene, but when heated together, form a product which only swells.   This cannot be caused by entanglement, as then it would be very unlikely that the system Oppanol-resin, entangled as it is (see the acetone-extraction curve), dissolves so rapidly in benzene.   Though the number of chemical bonds between rubber and resin may be limited, it must be concluded that such bonds are formed on heating rubber with a "vulcanizing" resin.
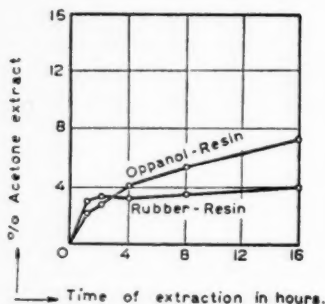
Fig. 6.—Extraction of rubber-resin and Oppanol-resin with acetone.
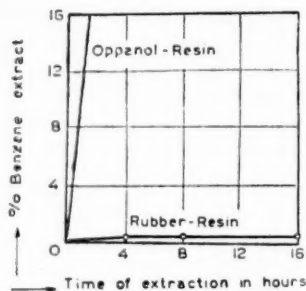
Fig. 7.—Extraction of acetone-extracted rubber-resin and Oppanol-resin with benzene.

The second question which remains is whether chemical combination between rubber and resin is the only reaction which takes place.   Considering the fact that the resins are thermosetting, this is very unlikely; probably there are more interlinking reactions between resin and resin than between rubber and resin.   The formation of water during vulcanization makes further condensation of the resin probable, while in some cases after vulcanization unmixing of rubber and resin is found.   This phenomenon can be due only to a resin-resin reaction, with exclusion of the rubber.

With the outline of the mechanism of reaction clear, a picture can be developed of the configuration of the rubber-resin vulcanizates.   The rubber molecules, forming an irregular knot of entangled thread molecules[17], are mixed with the resol molecules and then heated.   Two reactions are certain: the resol molecules condense to resin thread molecules—for in most cases the resin-forming phenol will have only two reaction-favorable positions in the nucleus—and in some places interlinking spots are formed between resin or resol and rubber.   It is not possible to detect whether interlinking spots are also formed between rubber and rubber, as is sometimes suggested for rubber-sulfur vulcanization.   The role of the magnesium oxide is not yet clear.

It must be kept in mind that the resin molecules are probably considerably shorter than the rubber molecules, so that the effect of entanglement is lessened. But as the resin is formed in the knot of the rubber molecules itself, in most cases it will be thoroughly mixed with it.   Considering the fact that the tensile strength of a material like rubber is due to secondary valence forces[18], these forces, especially those between rubber and resin, are of more importance than

the number of interlinking spots. The elasticity, however, probably depends largely on the number of primary valence bonds. Though good elasticity can be obtained with a small number of interlinking spots, a certain number of primary bonds is necessary. With rubber-resin vulcanizates it is likely that the number of these bonds is about as great as with rubber-sulfur vulcanizates.

SUMMARY

Natural and synthetic rubber can be vulcanized with several vulcanizing agents other than sulfur, though sulfur and sulfur compounds are the only agents of practical value. A combination of rubber and synthetic resin can be successful only when chemical bonds are formed. It has been found that this is the case with certain synthetic resins, and that natural and synthetic rubber can be vulcanized with these resins, without adding any other agent or filler, in much the same way as with sulfur. An example of these resins is the resol from pentaphene (p–t-amylphenol) and formaldehyde. Data are given for the technical properties of rubber-resin vulcanizates. Catalysis or a similar effect is produced by magnesium oxide, which increases the tensile strength, while hexamethylenetetramine prevents the reaction.

Balata can be vulcanized with the same synthetic resins as rubber; with gutta-percha the effect of heating with rubber-vulcanizing resins is the same as with sulfur.

The probable configuration of the rubber-resin vulcanizates consists of two systems of entangled thread-molecules, which are interlinked at a limited number of points by primary valence bonds.

ACKNOWLEDGMENT

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[2] A clear survey is made by Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
[3] Weak agents, some borderline cases, according to Fisher.
[4] Dufraisse and Compagnon. *Rev gén. caoutchouc* **18**, 40 (1941).
[5] By sulfur is meant sulfur and(or) substances which furnish sulfur.
[6] For a general example, see French patent 804,552 and additional 48,977 by Beckacite, Vienna.
[7] Kurt Albert, Wiesbaden.
[8] Bakelite, Ltd., London.
[9] See French patent 804,552 and additional 48,977.
[10] 164 grams (1 mole) of pentaphene, 200 cc. of 30% aqueous formaldehyde, 66 cc. of 3 N NaOH and 66 cc. of water.
[11] A strip of rubber is stretched to 200 per cent and kept in this position for 24 hours. One hour after release the permanent set is measured in percentage.
[12] After stretching to 150 per cent.
[13] Chloroanil, British patent 390,045; Naugatuck Co.; lead peroxide, Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
[14] Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
[15] Park, *Ind. Eng. Chem.* **24**, 152 (1932); Van Rossem and Soudijn, *Gummi-Ztg.* **52**, 1070 (1938).
[16] Thanks are due P. Dekker of the Rubber Institute T.N.O. for the careful determination of the extraction data.
[17] See Kuhn, *Kautschuk* **14**, 182 (1938).
[18] Unpublished investigations.

CARBON BLACKS IN GR-S *

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Introduction.—The importance of different types of colloidal carbon as reinforcing agents for the butadiene-styrene copolymer, GR-S, has been stressed in recent papers. It has been shown that, to a first approximation, the effect of carbon blacks in this type of synthetic rubber is similar to that in natural rubber, but it has been shown also that the extremely low tensile strength and poor tearing properties of uncompounded vulcanized GR-S necessitates the addition of some form of carbon black to almost all types of compounds. The present paper considers the influence of carbon blacks in vulcanized GR-S compounds. Earlier papers[1] have discussed the effect of carbon blacks in natural rubber.

TABLE I

Name	Symbol	Grade	Mean particle diameter $m\mu$ (after Wiegand)	Specific surface sq. m. per g. (after Wiegand)
Medium thermal	MT	Thermax	274	10
Lampblack	—	English	97	23
Fine thermal	FT	P-33	91 (74*)	27 (36.5*)
Semireinforcing furnace	SRF	Furnex	80 (83*)	33 (31*)
Semireinforcing furnace	SRF	Pelletex	80	33
High-modulus furnace	HMF (1)	Kosmos-40	47‡ (41†)	56‡ (63†)
High-modulus furnace	HMF (2)	Philblack	47?	56?
Acetylene	—	Shawinigan	43	63
Fine furnace	FF	Statex-B	36	70
Easy-processing channel	EPC	Spheron-9	29 (30†)	92 (86†)
Medium-processing channel	MPC	Micronex	28	94.5

* Value reported by Wiegand and Ladd[2].
† Estimated values by author[4].
‡ These values were actually obtained on Statex-93, which is assumed to have the same average particle diameter and specific surface as Kosmos-40.

In Table I the carbons studied in the present investigations are listed, with particulars of their particle diameters and specific surfaces, as determined in the electron microscope and recorded by Wiegand[2]. Earlier data reported by Wiegand and Ladd[3] on some of the carbons are also included for comparison. Except in the case of P-33 the later values do not differ materially from the earlier ones which were made use of by the author[4]. Wiegand's later values are invariably adopted in the present paper, and the assumption is made that the particle size of any particular type of carbon from one source does not vary appreciably. The further assumption is made that the same type of carbon from two different sources e.g., Kosmos-40 and Statex-93, is similar in average particle diameter and specific surface-area. Neither assumption is fully justified, but it is thought that the variation is not great enough to have a profound effect on the conclusions reached. These conclusions are based mainly on mixings in which base stocks of the composition in Table 2 were employed.

TABLE II

	Stock A	Stock B	Stock C	Stock D
GR-S	100	100	100	100
Sulfur	1.5	2	1.75	1.5
Mercaptobenzothiazole	1.5	1.5	1.5	1.5
Diphenylguanidine	0.2	0.3	0.4	0.3
Stearic acid	1	1	1	1
Tackol	4	4	5	4
Zinc oxide	5	3	3	5

Mixing.—For Series 1, two batches of base stock A were mixed in a GK12 Baker Perkins internal mixer and blended. The various carbons in concentrations of 10, 30, 50, 70 and 90 parts by weight to 100 parts GR-S were added on a 16-inch mill. After 24 hours maturing, each batch was remilled by grinding four times through a calender.

In Series 2, base stock B was employed, and carbon loadings of 20, 40, 60 and 80 parts by weight to 100 GR-S were used. The mixing procedure was the same as for Series 1 except that the batches were mixed in a random order.

For Series 3, which consisted of mixtures of various carbons in different proportions with MPC (50 parts in all), base stock C was used, the mixing procedure being as for Series 1.

In addition the above 2-stage mixing process was compared in compounds containing MPC black with a 4-stage process as follows: (1) GR-S, black and softeners mixed for each batch on 12-inch mill; (2) grind twice through calender and other ingredients added on mill; (3) grind twice; (4) grind twice.

Twenty-four hours was allowed for maturing between each stage. Base stock D was used.

Rate of cure.—The speed of vulcanization has been judged by a number of factors, including tensile strength, modulus (elongation at a given load), hardness (B.S.I.) and permanent set (at 50 kg. per sq. cm.). The "corners" of the curves relating vulcanizing time to these three properties generally agree within reasonable limits, and give an indication of optimum cure. This is illustrated in Figure 1. The tensile strength of a GR-S compound may
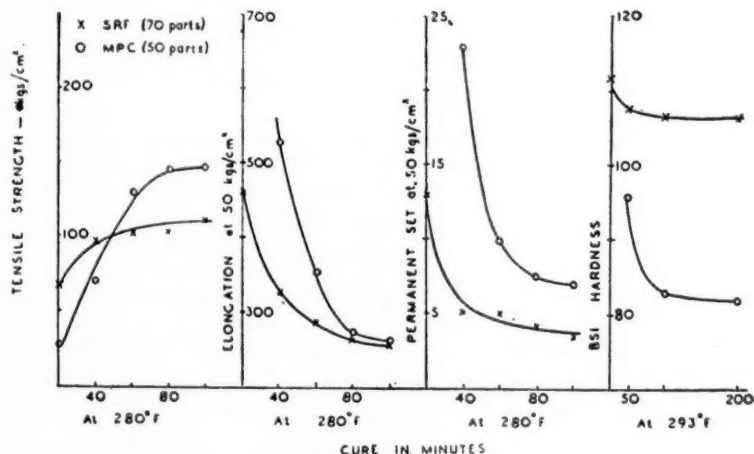
FIG. 1

approach its optimum while the modulus and hardness are still increasing fairly
rapidly, and the mere fact that the tensile has reached a high value does not
necessarily mean that the stock has had a full cure.   Resilience as a criterion
of rate of vulcanization is not, in general, so sensitive as it is with natural rubber
compounds, for the onset of high rebound is usually delayed until modulus and
hardness have reached steady values.   In general, high resilience persists over
a considerable range of cures.   Channel blacks invariably promote slower
rates of cure than any of the other carbon types.   The effect of cure on resilience
is illustrated in Figure 18.

Unless otherwise stated, the data on physical properties are given only at
the optimum cure.

Tensile strength.—The tensile data of GR-S vulcanizates tend to be rather
erratic, but there is usually a pronounced plateau effect in the tensile-cure
curves.   The most reliable figures are, therefore, obtained by averaging two
or three values in the region of the optimum.   The curves of Figure 2 were
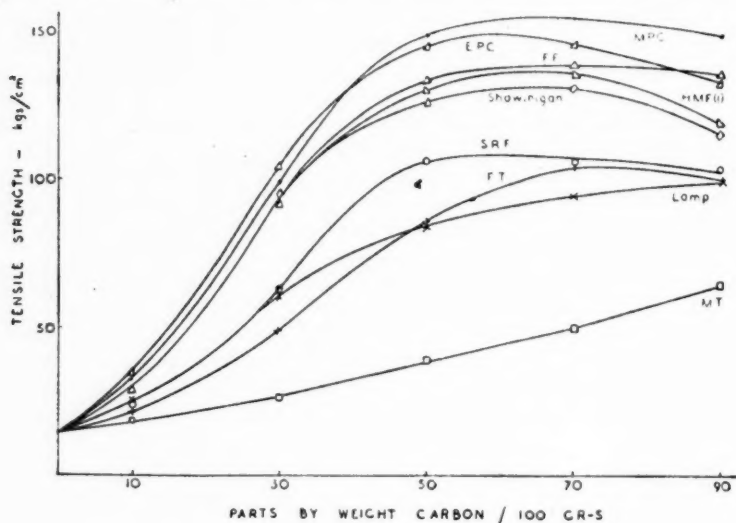
FIG. 2

derived in this way, and illustrate the results of tests carried out in Series 1
mixings.   They show (1) the extraordinary effect on tensile strength of all
kinds of carbon, a four-fold increase being achieved even by MT, a type which
does not appreciably influence the tensile of natural rubber; (2) tensile strength
increases up to concentrations of 50 to 70 parts by weight of carbon to 100 of
GR-S, and apparently has not reached its optimum at 90 parts loading in the
case of thermatomic, and (3) tensile increases in general as particle size of black
decreases, or as specific surface increases (see also Figure 3).

Tear resistance.—Tearing tests were not made in any of the Series 1, 2 or 3,
and the data plotted in Figure 4 on four carbons were obtained in an earlier
series in which the synthetic product used was Stanco.   The values indicated
should only be regarded as approximate.   They serve to illustrate the two
well-known principles; first, that channel blacks give the highest tear strength,
and, secondly, that tear resistance is much lower at 100° C than at ordinary
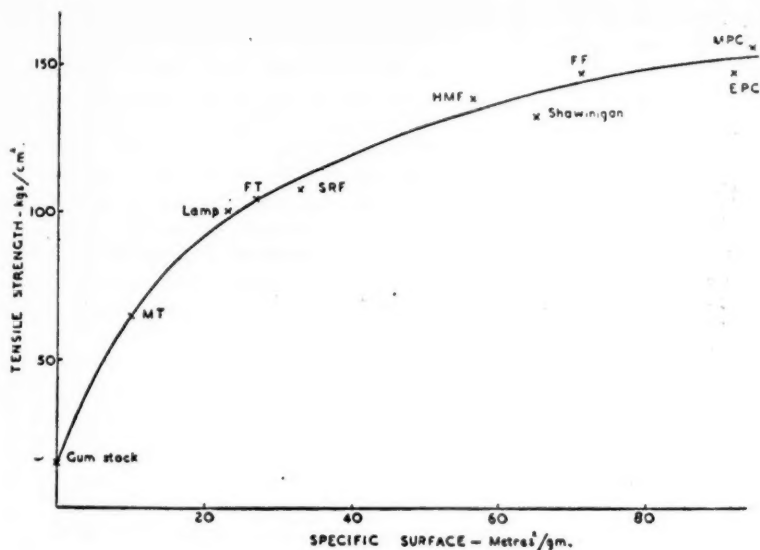
FIG. 3

temperatures. It should be added that the difference between the tearing strengths of GR-S and natural-rubber stocks of the types under consideration increases with increasing temperature. Thus, at 100° C the tear resistance of GR-S tread type compounds is low compared with that of natural rubber treads.

Abrasion resistance.—The Dunlop constant-energy abrasion machine[4] has been shown, in the case of natural rubber, to place the different colloidal carbons
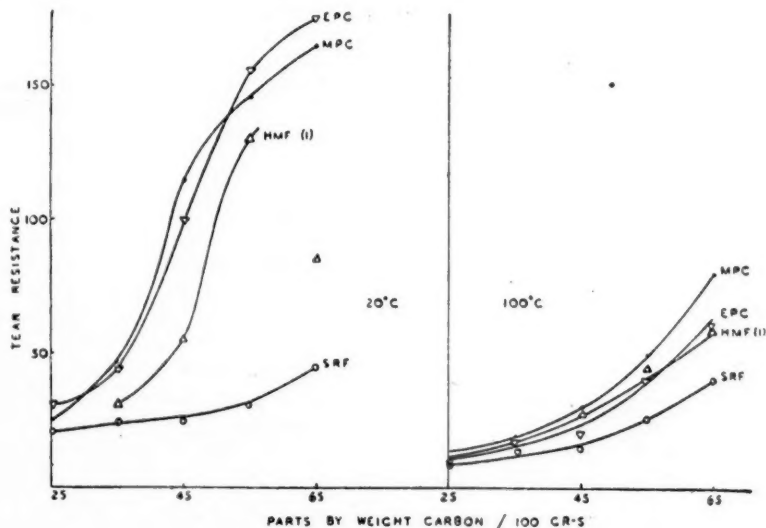
FIG. 4

in the true order of their effect on abrasion resistance and to line up quantitatively with wear resistance as measured on tires running on the road under ordinary service conditions. This abrasion tester shows GR-S carbon-loaded compounds to have abrasion resistance about 20 per cent superior to natural rubber similarly compounded. Comparison of GR-S and natural rubber tires on road-test, in general, have shown the former to wear somewhat more rapidly than the latter and, consequently, a correction factor has to be applied to the abrasion test results on GR-S stocks when comparisons are made with natural rubber. GR-S compounds compared among themselves on the abrasion machine, unless containing large quantities of softener or reclaim, conform to expectations, and the effect of the different colloidal carbons on the abrasion resistance of GR-S in general conforms to that of Hevea rubber. Figure 5
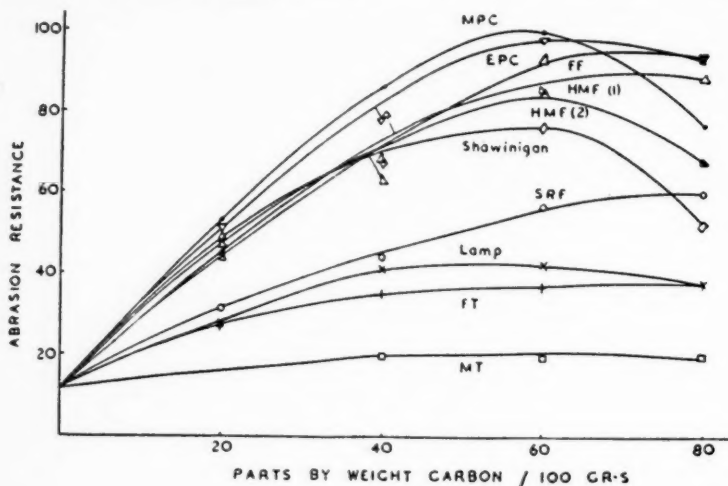
FIG. 5

illustrates the results of abrasion testing on Series 2 mixings, relative abrasion resistance, i.e., reciprocal of abrasion loss, based on a value of 100 for MPC at 60 parts loading being plotted against carbon concentration.
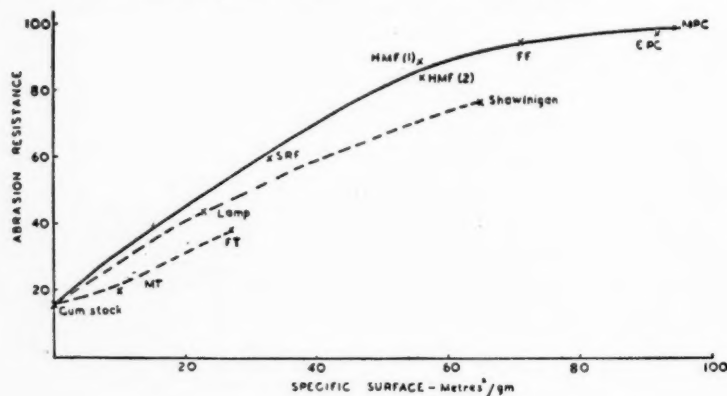
FIG. 6

The curves show optimum values at loadings of the order of 60 parts, but varying somewhat with the type of carbon. They suggest that figures at concentrations beyond the optimum are less reliable than those preceding it. Figure 6 shows a plot of abrasion resistance and specific surface. The points representing the carbons SRF, HMF(1), FF, EPC and MPC fall on an approximately smooth curve. These blacks all seem to belong to what has been termed the normal class[4]. The point representing HMF(2), a black which exhibits some degree of the property that has been named structure[2] lies below that denoting HMF(1). The structure carbons, lamp and acetylene, lie on another curve which represents a lower resistance to abrasion for a given surface area than that of the normal curve. The third class is represented by the thermal blacks, which, in relation to specific surface, have the lowest abrasion resistance of all the carbons tested.

The effect of mixtures of different blacks with MPC in a total concentration of 50 parts to 100 parts GR-S by weight (Series 3) is illustrated in Figures 7 and 8. In these curves abrasion loss is plotted against loading and surface,
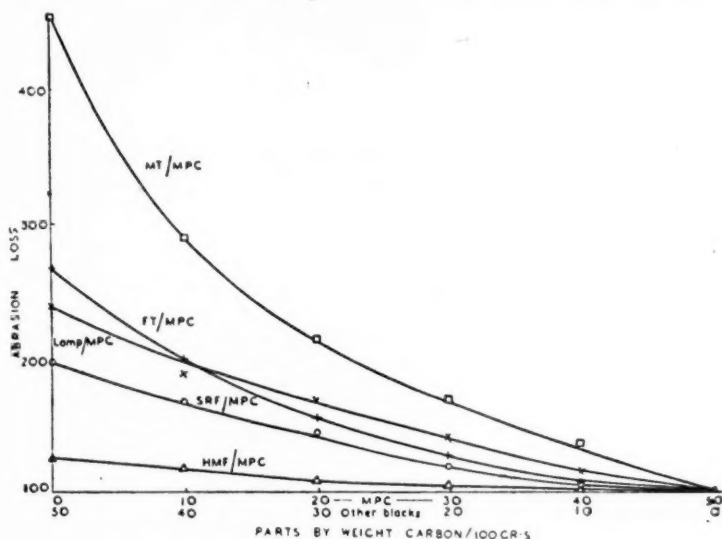
Fig. 7

respectively. The interesting point is brought out that abrasion resistance, even within the same carbon class, depends not only on the specific surface, but on the carbon mixture. Thus, mixtures of HMF and MPC give better abrasion resistance than those of SRF and MPC having the same specific surface. This result needs confirmation before it can be accepted as a general principle, but it may be significant that HMF has smaller particles than SRF. The curves further show increasing abrasion resistance in relation to specific surface in the order MT/MPC, FT/MPC, lampblack/MPC, SRF/MPC.

Stiffness and hardness.—Data on GR-S-carbon compounds in general confirm those obtained on natural rubber that modulus and hardness depend less on particle size than on other properties of the carbon. Resistance to stretch and deformation with any particular carbon increases with volume loading to
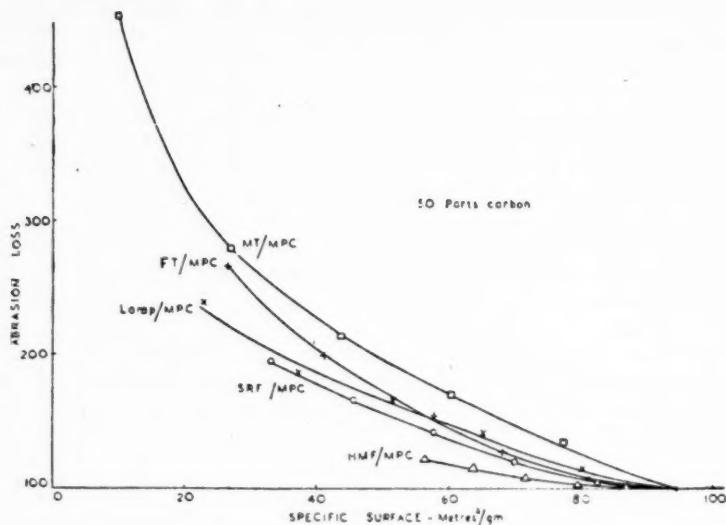
Fig. 8

points beyond the optimum tensile strength and abrasion resistance. The relationship between hardness (B.S.I.) and carbon concentration is illustrated in Figure 9. This graph shows that three structure carbons, namely, lamp-
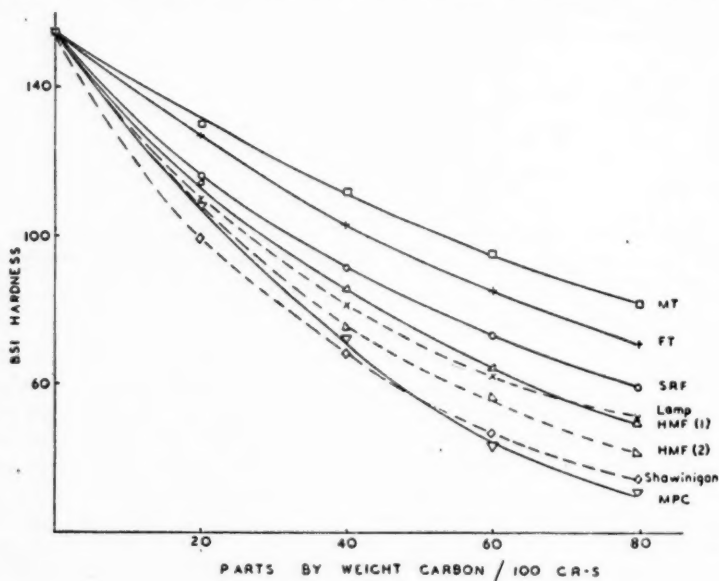
Fig. 9

black, HMF(2) and Shawinigan, though giving low indentation at moderate concentrations, tend to promote softer vulcanizates than might be expected at

high loadings. The hardness curves of these blacks flatten out more at high concentrations than do those of the others. The same effect in a less degree has been observed in natural rubber stocks. In Figure 10 (derived from Figure
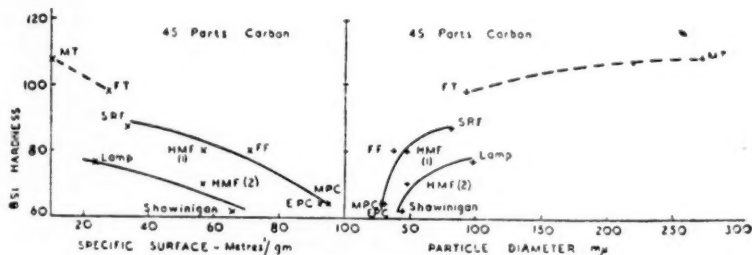
Fig. 10

9) and Figure 11 hardness and elongation at 50 kg. per sq. cm. are plotted, respectively, against specific surface and particle diameter. The points representing HMF(2) fall roughly into line on the curves connecting the other structure carbons. The further separation of the thermal carbons from the normal
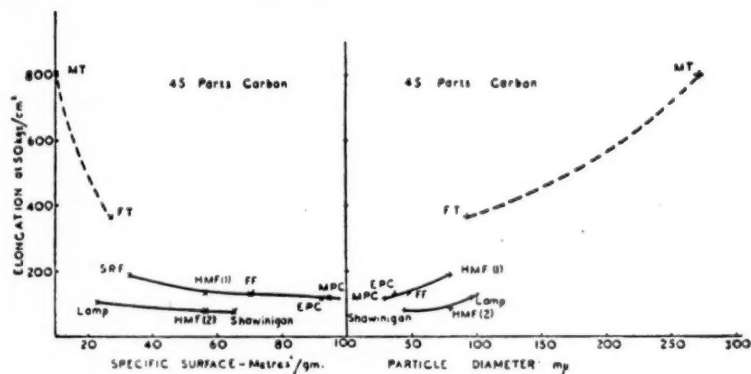
Fig. 11

carbons seems justified, and the most likely curves are drawn between the two points representing MT and FT. These results are in line with those on natural rubber, and separation of the blacks into at least three distinct classes[4] seems to be confirmed. It will now be shown, however, that such a separation is to some extent arbitrary, and that the HMF carbons show different degrees of structure formation.

Figure 12 illustrates the relation between hardness and loading of the Series 3 compounds incorporating mixtures of blacks. From these curves Figure 13 has been derived. At equal specific surface, lampblack/MPC mixtures promote greater hardness than do either HMF/MPC or SRF/MPC mixtures, in line with the greater structure forming tendencies of lampblack. The combinations MT/MPC and FT/MPC, as expected, produce softer vulcanizates at a given surface area than do the other carbons. A comparison of Figures 13 and 14 shows that, although the hardness curve of HMF/MPC

is close to that of SRF/MPC, the elongation curve of HMF/MPC closely follows that of lampblack/MPC. The effect of both lampblack and HMF, when added to MPC, is slightly to increase modulus. In this series of tests, there-
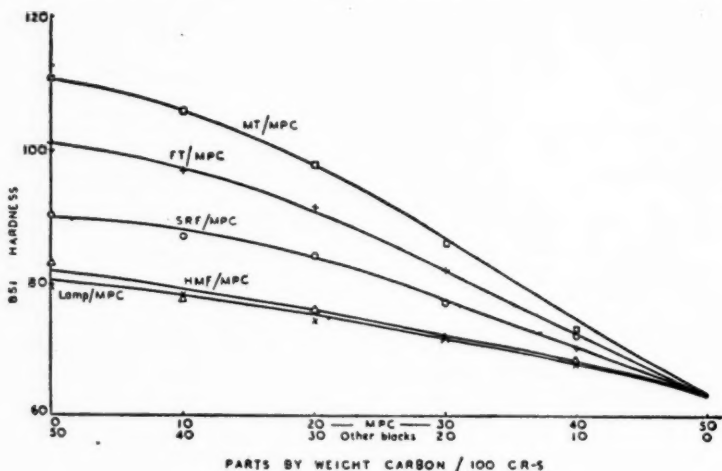
FIG. 12

fore, HMF(1) appears to act as a "normal" carbon with respect to compression stiffness and to some extent as a "structure" carbon in relation to extension stiffness. HMF(2) invariably seems to show a higher degree of structure than HMF(1). Wiegand's data[2] show that HMF (Statex 93) should be classed
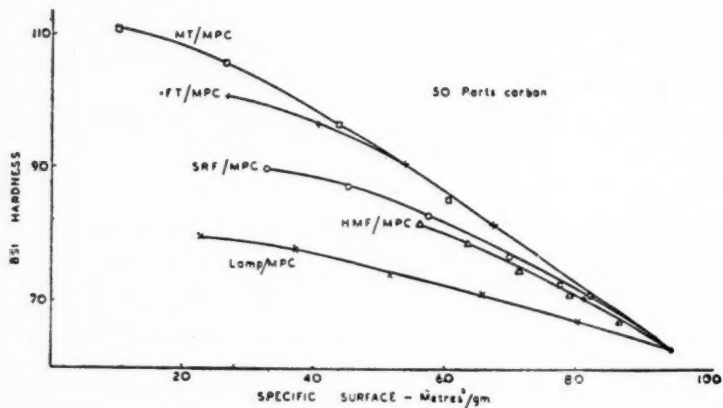
FIG. 13

as a structure carbon. The evidence taken as a whole indicates that there is no sharp distinction between "structure" carbons and "normal" carbons.

Resilience.—The rebound tests were made on the Healey (Dunlop) pendulum. The resilience of GR-S compounds under most, if not all, conditions is
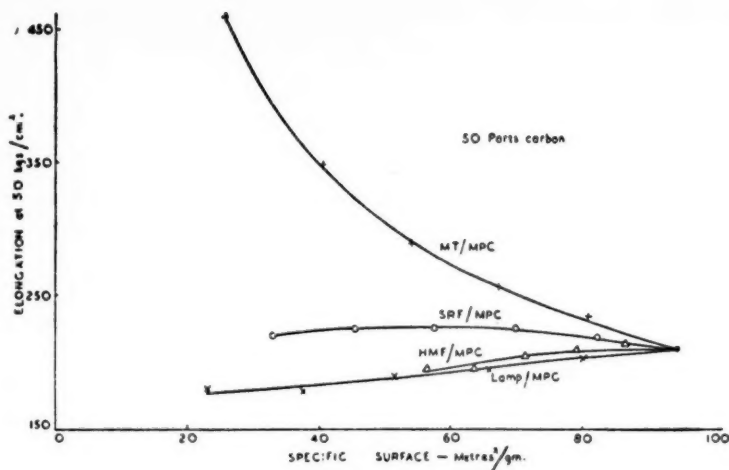
FIG. 14

lower than that of natural rubber compounds. In Figure 15 resilience-temperature curves of GR-S channel black compounds, including the gum stock (of Series 2) are compared with a similar series in natural rubber mixed, cured and tested during the same period. The points plotted are the optimum values,
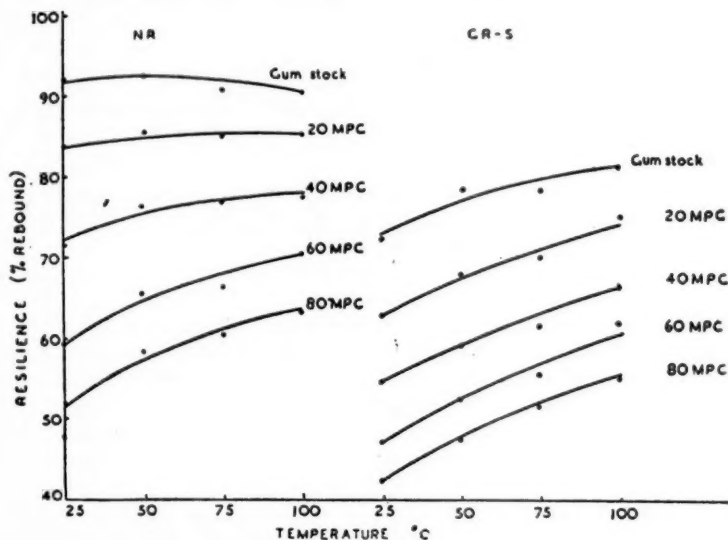
FIG. 15

which, in the case of Hevea, represent optimum cure, but for GR-S denote cures usually beyond the optimum as judged by other properties. It is seen that (1) the resilience of the unloaded natural rubber stock varies little between the limits of 25 and 100° C, (2) the slope of the rebound curves of Hevea

increases as carbon concentration increases, (3) the temperature of optimum resilience of natural rubber increases at least up to 60 parts loading (it is presumably higher than 100° C at concentration greater than 40), and (4) the resilience of all the GR-S compounds increases with temperature at approximately the same rate, which is greater than that of the highly loaded Hevea compounds. As the variation of resilience with temperature of natural-rubber compounds depends on sulfur and accelerator as well as on filler and concentration, it is reasonable to suppose that these factors operate similarly in GR-S, and therefore the curves depicted should not be regarded as necessarily representative of GR-S in general.

Rebound data obtained in the Series 2 mixings at 50° C are plotted against carbon concentration in Figure 16. In general, the linear relation found for
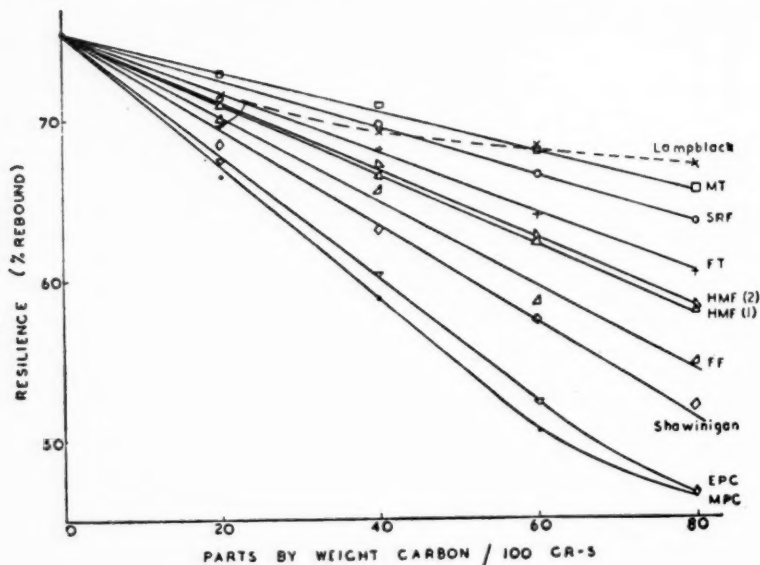
FIG. 16

natural rubber compounds holds for GR-S black-loaded stocks, but the rate of decrease is not so high. Two exceptions to the straight line law are found. The first of these refers to lampblack, the curve representing which is concave to the loading axis, and actually shows a resilience at high concentrations higher than that of the corresponding thermatomic black compounds. It is interesting to note that the same phenomenon occurred in the Series 1 mixes, but since an earlier investigation (on Hycar-OS30) had shown lampblack to behave normally, it was decided to look into the matter further by repeating the lampblack and thermatomic black mixings under carefully controlled conditions. The results are shown in Figure 17 and, although the lampblack points are somewhat erratic, they indicate the usual straight-line relationship. Microscopic examination of thin sections failed to reveal any differences in carbon dispersion between the lampblack stocks mixed at different times and if the unusual shapes of the lampblack curves in Series 1 and 2 mixings are due to a difference in the state of dispersion of the black it is on a sub-microscopic scale.

Figures 16 and 17 illustrate another departure from the linear relationship which connects resilience with carbon concentration. The channel black stocks up to loadings of about 60 parts behave normally, but beyond that point resilience falls less rapidly with increasing loading. The same effect was found in the Series 1 mixings and has been noticed in previous work; it appears to be general with GR-S. The phenomenon has not been observed with natural rubber channel-black compounds, but it seems likely that it might occur at
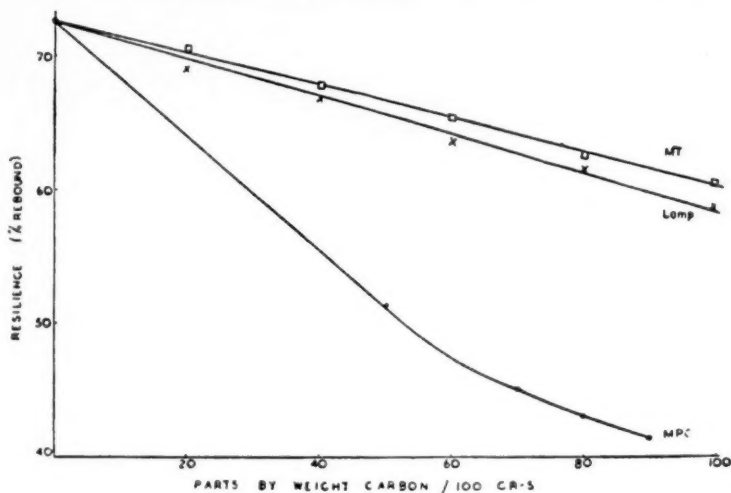
FIG. 17

still higher concentrations. The most likely explanation is a falling off in the degree of dispersion owing to difficulties of incorporating a large volume of black. In such circumstances the undispersed carbon acts as a diluent, with the result that the resilience of the mix is higher than would be the case if the carbon were in its usual state of dispersion. It is, of course, difficult to disperse channel black beyond loadings of 90 or 100 parts in natural rubber, and it is possible that the upper limit of satisfactory dispersion in GR-S is reached at a still lower concentration.

An attempt was made to improve the carbon dispersion by a change in the milling process, and Figure 18 compares the effect on resilience of the standard 2-stage and the 4-stage process outlined above. It is seen that, although resilience is modified by a change in milling technique, there is no change in the shape of the resilience loading curve.

The relationship between resilience and particle diameter in Series 1 and 2 is shown in Figure 19; a curve for natural rubber which is being included for comparison is derived from previous work[4] but the points of certain of the carbon types are altered to accord with Wiegand's most recent data[2]. The resilience values of Series 2 are taken from Figure 16; those of Series 1 have been similarly derived, the carbon concentrations in each case being 45 parts by weight, and the temperature of testing 50° C. As regards natural-rubber compounds, the new values of particle diameters have not modified the general conclusions beyond bringing acetylene black nearer in line with the other carbons and placing FT slightly out of line. The GR-S series both place

Shawinigan well below the curve, and, in the case of Series 2 (which is considered to be less liable to error than Series 1) FT is below the curve. The position of lampblack is interesting. Although imparting lower rebound than is ex-
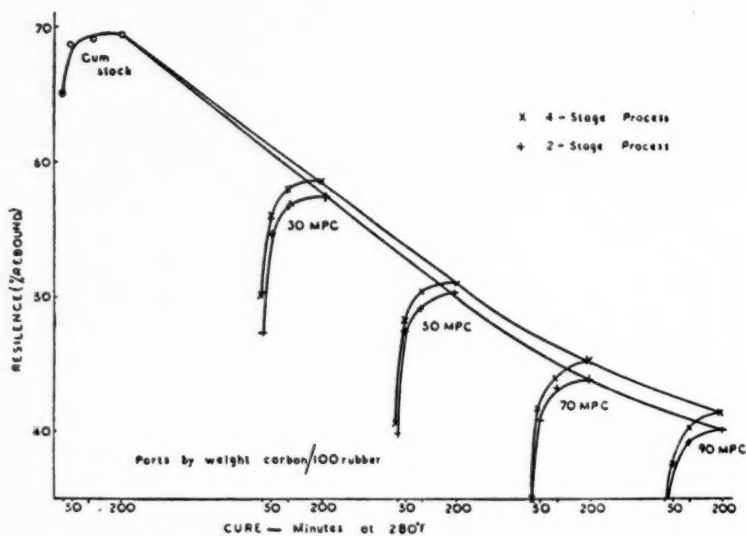
Fig. 18

pected from its particle size in natural rubber, it is shown to give normal resilience in GR-S. (At the 45 parts loading lampblack has the same relative position, whether derived from Figure 16 or 17).
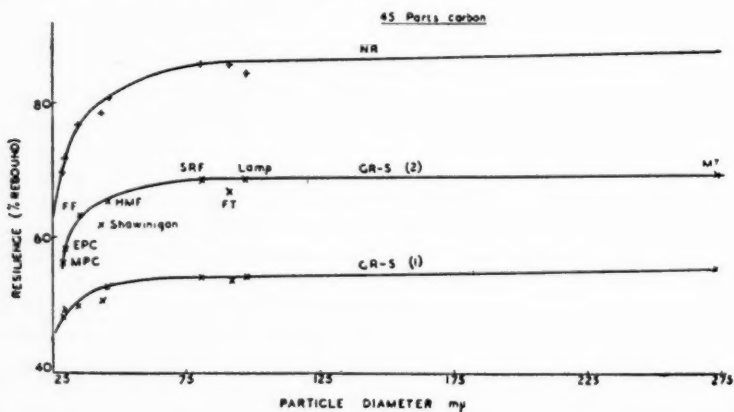
Fig. 19

In a paper by Cohan and Steinburg[5] rebound is stated to decrease linearly with particle size of carbon between 10 and 33 $m\mu$. Although this statement is true, it should be noted that the range considered falls entirely on one of the

two comparatively straight portions of a curve (Figure 19) which approximates to a hyperbola.

Resilience is plotted against specific surface in Figure 20 for both the natural rubber (N.R.) and GR-S (Series 2) compounds. The two curves, though of
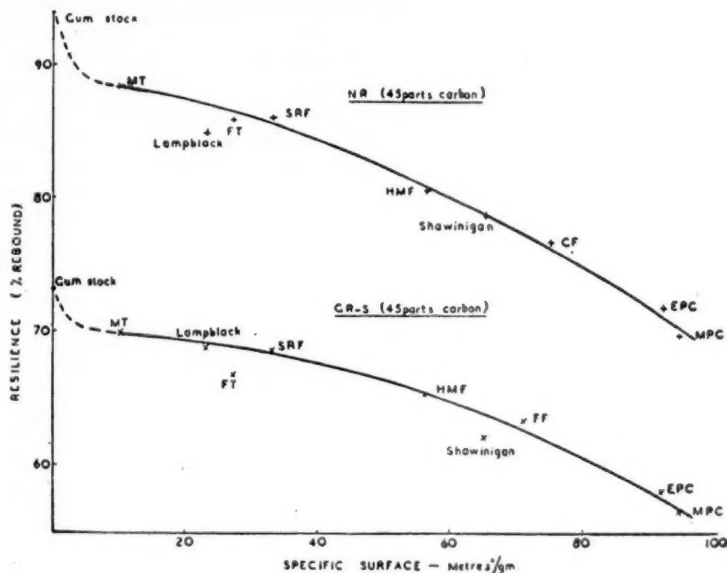
FIG. 20

similar shape, exhibit small differences of detail. It seems likely from the rebound figures that the assumed values of surface area for one or both the channel blacks (probably the value for EPC should be higher) are not quite correct, but whether this is so or not it does not affect any conclusions which can be deduced from the data. The difference between the two curves may be significant. Lampblack, as in the rebound curves, falls below the line with natural rubber, but on the line with GR-S. Acetylene black, though lying below the GR-S curve, falls on the natural rubber curve. FT lies possibly just significantly below the natural rubber curve, but very much below the GR-S curve. Both curves show the usual phenomenon of a sharp rise in resilience between the point represented by MT and the point of no loading.

Figure 21 depicts the resilience curves of the carbon mixtures of Series 3. Figure 22, which relates resilience to specific surface, is derived from Figure 21, and shows all the points lying very nearly on the same smooth curve, except those representing mixtures of FT and MPC. It seems evident, however, from the data on the "single" carbons that had the mixture of Shawinigan black and MPC been included in the series, this mixture also would have been represented by a curve lying below the normal curve.

The evidence above, taken as a whole indicates that carbon surface, either directly or indirectly, has a far greater influence than structure formation in determining impact resilience, whether in natural rubber or GR-S. All the carbons studied in the present and earlier investigations, with three exceptions, fall into line in this respect. As of these exceptions one (lampblack) is anom-

alous with natural rubber and the others (P-33 and Shawinigan) with GR-S, a single explanation such as the modifying effect of structure formation is inadequate. This question is discussed later.
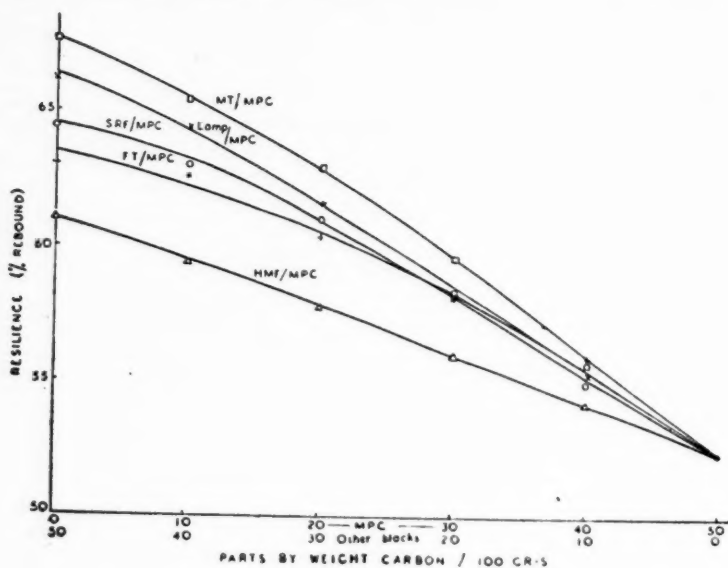
FIG. 21
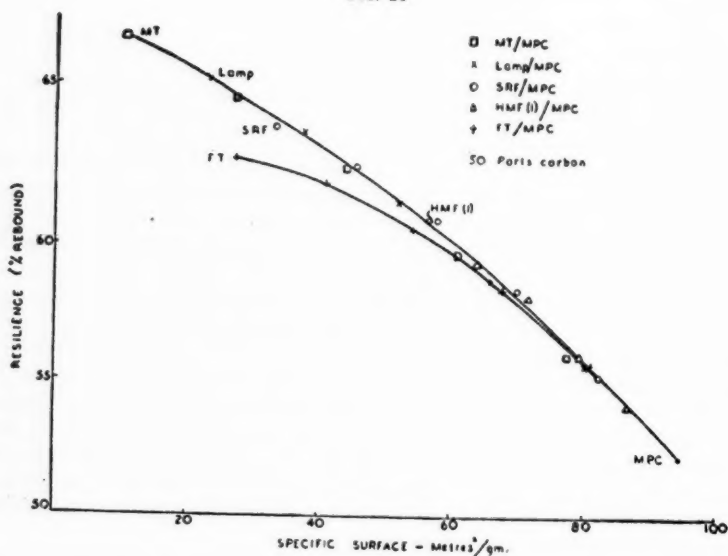
FIG. 22

Resilience and abrasion resistance.—It is of interest and practical importance to relate the resilience of mixtures of semireinforcing and other carbons with channel black to their abrasion resistance in GR-S compounds. This is done

conveniently in Figure 23.   The curves illustrate the principle that for equiva-
lent abrasion resistance a mixture of high modulus furnace and channel black
gives higher rebound than a mixture of semireinforcing furnace and channel
black giving the same abrasion resistance.   It will be evident that if it is
assumed that resilience is a measure of heat generation in a tire tread, then for
cooler running at equivalent wear rsistance, mixtures of HMF and MPC
(and presumably EPC) are to be preferred to mixtures of SRF carbons (includ-
ing lampblack) and channel carbons.   Also an all HMF tread is to be preferred
to the equivalent mixture of channel and SR.   This assumption is only fully
valid when treads of equivalent hardness are compared.   Actually, the mixtures
under consideration give rather softer vulcanizates than do all channel black
compounds.   The increased deformation to which such treads would be sub-
mitted would slightly increase their tendency to generate heat, but this effect
would probably be small compared with that of resilience.
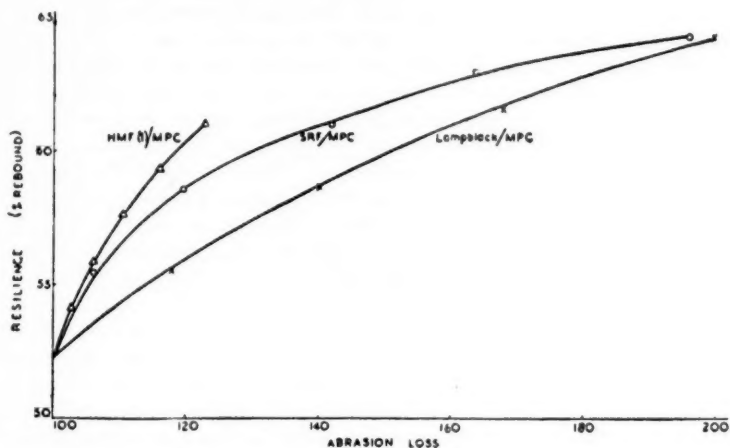
FIG. 23

Light scattering by rubber-carbon compounds.—In previous papers[6] reference
has been made to the color by transmitted light of thin sections of carbon-
rubber compounds and its bearing on the particle size of the black.   It has
been assumed that between the limits of about 80 and 30 $m\mu$, where the trans-
mitted light gradually changes color from blue-gray to red-brown, the actual
color is a measure of particle diameter in accordance with Rayleigh's law.
Recent estimates of particle size[2] strongly suggest that properties of the particles
other than their size are operative in promoting light-scattering.   Thus, FT,
with an average particle diameter of 91 $m\mu$, transmits less blue and presumably
scatters more light than SRF with an average particle diameter of 80 $m\mu$.
Furnex and Gastex, in fact, do not seem to scatter any light at all, although they
have smaller particles than FT, according to recent data.   Further, the HMF
carbons transmit light of a similar color to acetylene black (Shawinigan),
although they possess somewhat larger particles.   Acetylene carbons with still
smaller particles than Shawinigan have been subjected to the usual microscopic
technique and found to transmit a similar color to Shawinigan.   This leads to
the tentative suggestion that the structural arrangement of the carbon particles,

as well as their size, influences their scattering power, and it would appear that the effect of structure, or flocculation is to decrease the tendency to scattering.

Aspects of reinforcement.—Most properties of vulcanized rubber, either natural or synthetic, show some dependence on the particle size and specific surface of the incorporated carbon. Earlier views on the reinforcing action of small particles in rubber were based largely on the hypothesis of surface-energy changes at the interface between the filler and the rubber matrix. As pointed out by Wiegand[7] these views were largely speculative and even contradictory. Surface energy changes are by definition reversible, and although such reversible changes probably occur to some extent, as the addition of fine powders to rubber is a case of immersion wetting, no evidence has been adduced that they have an important bearing on reinforcement. Wiegand[2] made a new theoretical approach to the problem with his "discrete rubber" theory, which imagines the rubber phase in structural units larger in general than the carbon particles. The latter are supposed to surround each rubber unit and function as bonds between adjacent units, and an additional number of carbon particles fill the voids between the rubber macromolecules. Although Wiegand's theory offers a better explanation of the facts than the earlier hypotheses, it seems to need some modification to accord with certain of the facts. x-Ray diffraction patterns, according to Gehman and Field[8] do not support this theory.

On any hypothesis it would appear that the carbon particles, or some of them, are attached to the rubber molecules. Naunton and Waring[9] suggest that reinforcement is a type of vulcanization in which the strong bond between rubber and carbon acts like a sulfur bridge. Thornhill and Smith[10] tested this hypothesis by unsaturation experiments, and arrived at the conclusion that if a chemical combination of the type suggested does occur, it cannot involve more than one or two double bonds out of every hundred. The fact that carbon black, when recovered from rubber vulcanizate is in its original form, is further evidence in favor of the view that reinforcement is a physical phenomenon. Amon, Smith and Thornhill[11], who have found that channel black can be recovered both quantitatively and with unchanged surface area from vulcanized rubber, point out that this need not necessarily be interpreted as evidence of complete lack of surface reactions. Clark and Rhodes[12] conclude from x-ray studies that carbon black exists in rubber as a physical dispersion; while admitting the possibility of powerful adsorptive forces. Weiss[13] points out that, according to modern valence concepts, no sharp distinction can be made between the physical van der Waals forces and true valence forces.

There is a considerable body of evidence pointing to the conclusion that the forces between carbon-particle surfaces and rubber molecules are not, in part at least, of a high order. An instance of weak bonding between carbon particles (FT) and rubber surfaces has recently been actually observed by Ladd[14] in the electron microscope. The well-known phenomenon of flocculation of channel black particles in unvulcanized rubber compounds strongly suggests that, under some conditions at least, the forces between carbon-rubber surfaces are not so great as those between carbon-carbon surfaces. This flocculation of channel black into structures, presumably similar to those characteristic of lamp and acetylene black, points to the probability that all colloidal carbons show some tendency to structure formation in rubber. This view is supported by electrical conductivity considerations[15]. The effect is least pronounced in the thermal carbons, as is evidenced by their small effect on modulus. Electron micrographs recently reproduced by Wiegand[2] show FT particles individually

dispersed in a rubber cement, after being milled into rubber. Wiegand further shows, by an electron micrograph of Shawinigan acetylene black in rubber cement, and from modulus considerations in Perbunan compounds, that the original chainlike structure present in this type of carbon persists after the milling treatment. An electron micrograph of a torn surface of vulcanized rubber has recently been produced by Drummond and reproduced by Bulgin[15], which actually shows chains of Shawinigan black particles. Such networks do not appear to be characteristic of either dry or wet dispersions of channel blacks, but, as mentioned above, they are presumed to exist when the carbon is dispersed in rubber.

The flocculation of channel black particles is attributed by Bulgin to Brownian movement of the particles, which, when they come into sufficiently close contact with each other, coalesce because of the free forces existing at their surfaces. The conception of Brownian motion in an apparently "solid" medium such as rubber, is rather startling, but Bulgin argues, by the application of Einstein's equation to the observed values of the time required for the electrical resistance to reach a constant value, that such a concept is justified on the assumption of a microviscosity for rubber considerably less than that of the macro-value.[16]

Causes of stiffness in vulcanized rubber.—Some authors regard the stiffening effect of carbon blacks in natural and synthetic rubber as synonymous with the reinforcing effect. It has been argued by the author[4] that stiffness and reinforcement are, in part at any rate, the expressions of different mechanisms. Stiffness, of course, always accompanies carbon reinforcement, but it increases with carbon concentration to loadings considerably beyond the optimum for such properties as tensile strength and abrasion resistance. It shows little change with change in particle size, and is greatest in compounds having high structure-forming tendencies, but lower tensile and abrasive properties than would be expected from particle size considerations alone.

As a result of electron microscope studies Hall, Hauser, Le Beau, Schmitt and Talalay[17] have concluded that rubber has an affinity for carbon surfaces which provide points of attachment for rubber chains. These authors suggest that the constraints resulting from this attachment have the effect of increasing the modulus, since this property depends to a large extent on the relative freedom of long chain segments. This hypothesis accords with the so-called plastic solid film theory which Spear proposed as long ago as 1923[18]. Spear pointed out that if rubber is adsorbed on the carbon particles the portion on the immediate surface ought to have less extensibility than the rubber, and be more resistant to distortion than the matrix would be in the absence of a filler. The x-ray studies of Gehman and Field[8] have also supported Spear's hypothesis, these authors having interpreted their x-ray diagrams (which show that the effect of carbon black is to spread the spots into arcs) in terms of a field of enhanced stress in the vicinity of the carbon particles. Recently Gehman[19] has extended this theory by mechanical considerations. He makes the assumption that the films of rubber presumed to exist between the particles are attached to the particles, and shows from considerations of packing that the thickness of the rubber film between particles for any given volume loading is proportional to the particle diameter. Under such circumstances the stiffness under compression would be expected to increase with carbon concentration, and it is shown that the films act as restraining surfaces, and that the conditions are analogous to those existing when a test-piece in compression has a high

shape factor, *i.e.*, a high load area/free area. Load-compression curves of GR-S compounds containing various carbon blacks show good agreement with theory. Gehman's curves show that the variation in stiffness is small compared with the variation in particle size, but they do show a limited dependence of the compression modulus on the particle size for a given volume loading.

This picture of equally spaced rows of particles separated by films of rubber explains the dependence of stiffness on volume loading, but Gehman mentions that "variations from results to be expected on the basis of a straightforward shape factor interpretation might occur for a number of reasons. Among these should be mentioned particle size distribution, particle shape, and especially pigment dispersion." It is evident that the type of carbon dispersion which consists of a network of strings of particles virtually in contact, will have a different influence on the stiffness of the compound than one in which each particle is insulated from its neighbor by a film of rubber. It is further evident from the data recorded in the present and other papers, and in particular those of Wiegand, that this influence is in the direction of increased stiffness. As this structural network may be presumed to be three-dimensional, it should have the effect of increasing the rigidity of the rubber-carbon structure as a whole. It may, therefore, be assumed that the stiffness of a rubber (or GR-S) compound reinforced by the incorporation of a carbon with structure-forming tendencies, depends partly on the enhanced stress in the vicinity of the carbon particles attached to the rubber chains; in other words, on the Spear effect, and partly on the rigidity of the carbon-carbon structure.

The degree of structure varies from black to black. A clue to the cause of these differences in structure-forming tendencies is found in electron diffraction[20] and x-ray diffraction[21] studies, which indicate that carbon blacks are two-dimensionally crystalline, consisting of a few parallel graphitic layers in random, or "turbostratic" orientation. Biscoe and Warren[21] show further, by small angle scattering, that the actual carbon black particles consist of clusters in random arrangement of such turbostratic crystallites. Rossman and Smith[22] by combining the x-ray data of Biscoe and Warren with density determinations made by helium displacement, calculated the free space within the particles, and thus found the separation between the parallel layer groups to be much greater in acetylene (Shawinigan) black than in channel black (Spheron-6). The authors suggest that the porous nature of acetylene carbon may, by the presence of residual forces, induce a secondary association of particles, and consequently a high electrical conductivity. Bulgin, in a paper to be published, has produced curves which suggest that both electrical resistance and hardness (B.S.I.) of carbon loading compounds are considerably influenced by crystallite size at carbon concentrations which give the same mean separation of the particles.

Comparison of the behavior of colloidal carbon in GR-S and Hevea in relation to reinforcement.—Broadly, the effects of carbon blacks in GR-S parallel those in natural rubber, any differences being for the most part in degree rather than in kind. But these differences are important, not only on practical grounds, but in their bearing on the theoretical aspects of rubber compounding, such as the mechanism of the action of small particles on the various properties. The most obvious difference between gum stocks of GR-S and natural rubber is the extremely low tensile strength of the former compared with the latter. Natural rubber is used for many purposes without carbon reinforcement, but

in the case of GR-S the addition of a substantial volume of some form of carbon is nearly always a necessity. It is a remarkable fact that a fully reinforcing carbon gives a more than 1000 per cent increase in tensile strength compared with a mere 50 per cent increase in Hevea.

The low tensile strength of GR-S is probably in part, if not wholly, a consequence of its inability to become fibrous or crystalline on stretching. Natural rubber becomes stronger as it is stretched, and in the words of Fielding[23] "its resistance to rupture or tear is increased by the very force or deformation that tends to rupture it. At the same time it becomes weaker in a direction at right angles to this. The result is that tensile strength is high whether or not a reinforcing pigment is used, and rubber may be said to be reinforced by its own crystallization." Fielding remarks that the action of carbon black in GR-S is thought to be the same as in natural rubber, but as "natural rubber can crystallize it is already well bound together and the possible increase in tensile is not so great as it is with GR-S." This view is supported by Cohan and Steinburg[5].

The tensile and tear strengths of carbon-loaded GR-S compounds fall off much more rapidly with increasing temperature than do those of Hevea compounds, which, on the assumption of adsorptive attachment, may mean a reduction in carbon-GR-S bond strength as the temperature rises. This might be expected in view of the probability discussed above of a comparatively low degree of bonding between carbon particles and rubber molecules.

Enhanced tensile strength is one aspect of reinforcement, increase in abrasion strength is another at least as important. The resistance to abrasion of vulcanized Hevea gum stocks is not greatly superior to that of GR-S gum stocks, but the addition of 50 parts channel black (by weight of polymer) increases the abrasion resistance of rubber four- or five-fold, and that of GR-S about six-fold. The action of carbon black in increasing the abrasion resistance would thus appear to be similar quantitatively in natural and synthetic rubber. This may mean that the mechanism which increases tensile strength is not wholly the same as that influencing abrasion. It seems probable that the effect of carbon blacks on the abrasion resistance of GR-S and Hevea compounds is similar because abrasive strength has no dependence on crystal formation or fibering of the polymer. One would imagine that the deformations to which the surface of a rubber tread is subjected when tires are running on the road are not high enough for fibering to take place. Similar conditions apply to abrasion testing in the laboratory. Unlike the case of tensile strength there would then be no reinforcement by crystallization.

The mechanism of abrasion resistance is evidently complicated. Figure 6 shows that carbons of both high and low structure-forming tendencies fall below the normal abrasion line. It has been suggested by the author[4] that the poor abrasion resistance, relative to particle size, given by FT might result from its known low activity per unit area of surface. Or it may be a consequence of its lack of stiffening power, which results from a low degree of structure formation, since although abrasion resistance shows no direct relation to modulus or hardness, experience suggests that some rigidity is necessary to achieve high abrasive strength. The mechanisms causing high stiffness, which have been discussed in the foregoing pages, almost certainly operate in improving abrasion resistance up to a point, but as the stiffest compounds are not those with the highest abrasion resistance, an additional factor at least is needed for an explanation of the phenomenon.

The author[4] has given reasons for the view that the high abrasive strength of carbon-reinforced rubber compounds might result from the strong bonding of a limited number of particles to the molecules of the polymer. Researches referred to in previous pages, though leading to the conclusion that carbon black exists in rubber (and presumably in GR-S) as a physical dispersion, do not preclude the possibility of a limited number of chemical (or chemisorptive) bonds connecting the carbon particles to the polymer chains. These may be primary valence linkages, as suggested by Naunton and Waring[9]. It is presumed that optimum abrasion resistance coincides with the saturation point of these bonds. Their number, at a given carbon concentration, increases with increasing number of particles, that is, as particle size decreases. On this view abrasion resistance is a function of at least three variables; (1), a chemical, or powerful chemisorptive bond between carbon and rubber of a small proportion of the particles; (2) enhanced stress in the rubber (or GR-S) in the vicinity of the carbon particles due in the main to the restraining influence of relatively weak adsorption forces between carbon and rubber, and (3) the influence of carbon-carbon structures.

Some of the differences between the effects of colloidal carbon on Hevea and GR-S have been attributed to the differences between the particle sizes of Hevea and GR-S latices. The electron microscope shows the average diameter of Hevea latex particles to be of the order of one micron, while that of a GR-S latex particle is nearly 20 times shorter. Wiegand points out that his discrete rubber theory rests on the assumption that the rubber units are larger than the carbon units, and that it needs modification in the case of some synthetic rubbers. "Depending on the relative size of the rubber and carbon units, either discrete carbon or discrete rubber conditions may apply. This suggests a point of inversion as the rubber and carbon units become similar in size." He cites evidence in support of this phase inversion concept, and in particular refers to the much larger ratio between SRF and EPC resistivities in coarse than in fine polymers. This is explained on the assumption that the SRF carbon chains are better insulated by the polymer particles when the latter are the more finely divided. It should be noted that the considerably higher resistivities of lampblack-GR-S than lampblack-natural rubber compounds[15] conform to Wiegand's hypothesis.

It is possible that some of the anomalies between GR-S and Hevea compounds noted in the present study might be explicable on the hypothesis of differences in size of the polymer units. Thus, lampblack gives a relatively higher resilience, and Shawinigan and FT a relatively lower resilience in GR-S than in natural rubber. Lampblack particles are much smaller than Hevea latex particles and larger than GR-S latex particles, whereas Shawinigan black particles are a little smaller than GR-S latex particles. Both these blacks develop a high degree of structure the effect of which might be modified, as suggested by Wiegand, by the size of the polymer unit, though in what way resilience would be affected is not clear. FT particles are much smaller than Hevea latex particles and larger than GR-S latex particles. This black differs from lamp and acetylene carbons in having very low structure forming tendencies.

Such suggestions as these are little more than speculations in the present state of knowledge. The development of an improved technique of electron microscopy, whereby outlines of the structure of the polymer-carbon complex can be observed, will throw further light on the problem.

Summary and conclusions.—The behavior of colloidal carbon in GR-S follows closely its action in natural rubber, though there are important differences of degree. Among the properties which have been studied, tensile strength, tear resistance and resilience, with one or two exceptions, show a close relationship with the particle size and specific surface of the carbon. Abrasion resistance depends mostly on particle size, but the effects are modified by the degree of structure formation. Modulus, both of extension and compression, shows little correlation with particle size, but has a high dependence on structure. The carbon concentrations at which tensile, tearing and abrasive strengths reach optimum values are, in general, higher in GR-S than in Hevea rubber.

The agreement between the action of carbon blacks on the tensile strengths of Hevea and GR-S is only qualitative; on abrasion resistance it is quantitative, probably because polymer crystallization is not involved under the conditions of abrasive wear. Certain differences between the effect of carbon blacks in the two polymers have been noted which might be ascribed to other properties of the hydrocarbon than the presence, or absence, of crystallization or fibering. These may be concerned with the size of the polymer units, which Wiegand has suggested are very much smaller in GR-S than in Hevea.

The present study has confirmed former conclusions drawn from data on natural rubber compounds that the carbon blacks can be grouped into different classes according to the manner in which certain physical properties relate to particle size, but it has been shown that the line of demarcation between these classes is less rigid than was formerly thought. This slight modification of viewpoint results from the introduction of new types of furnace black with varying degrees of structure formation.

The data accumulated in this and earlier investigations, combined with the conclusions and theories of other authors, lead to the suggestion that the stiffening effect in natural and synthetic rubber depends partly on enhanced stresses in the rubber contiguous to the carbon particles and partly on the rigidity of the carbon-carbon structure. There is good evidence that the carbon-carbon forces are in some instances more powerful than the carbon-rubber forces.

The influence of carbon blacks in improving abrasion resistance depends mainly on a limited number of powerful chemisorptive bonds (or even valence linkages) between the polymer molecules and the carbon particles. These forces increase with increasing volume loading and with decreasing particle size until the bonds are saturated. The mechanisms which cause stiffness will also have some effect in increasing resistance to abrasion, but beyond a certain point the stiffening factors seem to operate in the opposite direction.

ACKNOWLEDGMENT

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THE EFFECTS OF PROÖXYGENIC SUBSTANCES ON RECLAIMED RUBBER *

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INTRODUCTION

In a paper entitled "Reclaimed rubber mixtures without new rubber" (*India-Rubber J.* **103**, No. 20, p. 9, August 22, 1942), Ghez has described the use of cobalt linoleate for plasticizing reclaimed rubber, without, however, giving any details as to the way in which this compound was used for the purpose. This application of a proöxygenic compound offers interesting possibilities, both from the practical and the theoretical points of view. Furthermore it is often difficult to calender reclaimed-rubber mixtures containing no new rubber smoothly, and an effective peptizing agent for reclaimed rubber would be highly useful as a practical aid in processing. Then again, a peptizing effect of proöxygenic substances might explain the part played by oxygen in the mastication of reclaimed rubber.

INFLUENCE OF PLASTICIZATION

In the experiments carried out in the present investigation, the procedure was as follows.

Two-hundred grams of reclaimed rubber manufactured by the alkali process (the Plastex grade of Wattelez) was masticated cold for 5 minutes on a laboratory mill (friction ratio 1:1.35 and surface speed of 3.14 meters per minute); at the end of this time, 1 per cent of proöxygenic compound was added, the mixture was milled for another 5 minutes, was allowed to rest for 24 hours, and finally was milled a third time for 5 minutes. A control sample was put through the same procedure, but without the addition of any proöxygenic compound. It was not feasible to prolong the time of milling beyond fifteen minutes, because the samples of reclaimed rubber which contained proöxygenic compounds commenced, after this time of milling, to stick to the mill rolls. After a second rest of twenty-four hours, the Williams plasticity values of the reclaimed-rubber mixtures were determined. Test-specimens 2 cc. in size were cut from a slab which had been pressed cold. The temperature used for measuring the plasticities was 70° C. The load was 5 kilograms. The plasticity reading was Y.5, 5 minutes after application removal of the load.

A comparison of the plasticity readings thus obtained (see Table) shows that, of the four proöxygenic compounds which were tested, none had any influence on the plasticization of the particular reclaimed rubber which was tested.

This is a rather surprising fact, since, as judged by hand, the reclaimed-rubber samples containing the proöxygenic compounds seemed to be softer than the control sample containing no such agent. The samples containing proöxygenic compounds were also more tacky than the control sample, and the sample containing copper linoleate was the most tacky of all. It should, however, be

EXPERIMENTAL RESULTS

Measurements	Control with no agent	Cobalt stearate	Cobalt linoleate	Copper stearate	Copper linoleate
Plasticity (Williams Y.5)	6.03	6.25	6.09	6.02	6.18
Elastic recovery (Williams R.5)	3.31	3.40	3.42	3.21	3.17
Hardness (Shore)	75–73	75–73	75–73	75–73	75–73
Tensile strength (kg. per sq. cm.)					
before aging	65	65	62	65	66
after 14 days in Geer oven	63	62	60	67	69
after 28 days in Geer oven	61	59	58	66	68
Extensibility (percentage)					
before aging	275	270	270	280	280
after 14 days in Geer oven	135	130	130	160	150
after 28 days in Geer oven	105	95	100	130	120

added that the surfaces of the reclaimed-rubber samples which contained proöxygenic compounds were not any smoother than the surface of the control sample.

EFFECTS ON AGING

The results of these experiments suggested a further study to determine the influence of proöxygenic compounds on the aging of a reclaimed-rubber mixture containing no new rubber. To this end, each of the five mixtures already described was used to prepare five vulcanizates of the following composition:

Reclaimed-rubber mixture (containing proöxygenic compound)	101
Sulfur	1
Mercaptobenzothiazole	0.5
Butyraldehydeaniline	0.5
Stearic acid	1
Zinc oxide	10
Carbon black (CK-3)	10

The mixtures were vulcanized in a press for 20 minutes at 143° C. They were then aged, in the form of Schopper rings, in a Geer oven at 70° C.

The dynamometric measurements before and after aging (see Table) show that, contrary to what takes place in the case of crude-rubber mixtures, proöxygenic compounds have practically no influence on the aging of reclaimed-rubber mixtures containing no new rubber. It should be noted that, after aging, the vulcanizates which contained copper salts had physical properties even superior to those of the control sample containing no proöxygenic compound.

CONCLUSIONS

It might at first be assumed that antioxygenic compounds originally present in scrap rubber used in the manufacture of the reclaimed rubber would be sufficient to explain the extraordinary resistance of the reclaimed rubber to the action of proöxygenic compounds. It is, however, highly improbable that these antioxygenic compounds survive caustic soda treatment at 190° C. On the other hand, a crude-rubber mixture, even when protected by an antioxygenic compound, never shows such great resistance to proöxygenic compounds as that shown by the reclaimed-rubber vulcanizates described in the present work. It seems probable, therefore, that this insensitivity of reclaimed rubber to proöxygenic compounds, both during plasticization and during aging after vulcanization, is in some way connected with the actual chemical structure of the reclaimed rubber itself.

SHELLAC AS AN INGREDIENT OF RUBBER COMPOSITIONS *

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INTRODUCTION

The possibilities of shellac as an ingredient of rubber compositions seem to have attracted considerable attention, particularly among inventors, judging by the large number of patents for the preparation and use of compositions containing rubber or gutta-percha and shellac. Many of these patents relate to unvulcanized compositions used, either solid or in solution, as cements or adhesives, coating, waterproofing, or impregnating compositions, mouldable plastics and electrical insulating materials, though it seems doubtful if many of these ever attained any commercial importance.

In recent years some attention has been given to shellac-latex compositions, particularly for making waterproof and greaseproof paper, and to solid rubber-shellac mixtures prepared therefrom and used, for example, for golf-ball covers.

Judging by the literature, the use of shellac in vulcanized rubber has not received so much attention, though it is understood that fairly large amounts are used in the United States of America, particularly for rubber soles and heels, flooring, matting and tiling, moulded and mechanical goods, extruded tubing and cable insulation, composite rubber-fabric particles, packings and ebonite. Nevertheless there is surprisingly little precise information as to the technical advantages that have led to these uses. All that can be deduced from published experimental data[1] is that shellac lowers the tensile strength and breaking elongation, and makes the rubber harder and stiffer but less resistant to the swelling action of gasoline. Statements, unsupported by data, have been made to the effect that shellac acts as a softener, which facilitates extruding, calendering, and moulding; improves surface finish; reduces porosity; renders the vulcanizate more resistant to heat, aging, water, and swelling by hydrocarbon liquids, and less permeable to gases; and improves its electrical properties[2].

A recent patent[3] claims that shellac has an especially great hardening effect in mixings containing basic oxides. Another[4] refers to the use of shellac in mixings free from alkaline materials and containing only nonalkaline accelerators; in keeping with this is the statement[5] that, in presence of shellac, acidic accelerators give the best results.

It seems from this brief review that in the rubber-shellac field, scientific investigation has lagged far behind the practical man's "rule of thumb" and the inventor's imagination. If any considerable progress is to be made in the application of shellac in rubber manufacture, it is obvious that at least the basic data concerning its effect on the properties of the unvulcanized stock and the vulcanizate should be determined and made widely known.

It was primarily with the object of obtaining such data that the present investigation was undertaken. Most of the work was concerned with mixings to be used in the vulcanized state, but some interesting observations on the properties and possible uses of unvulcanized rubber-shellac mixtures are recorded. The investigation is not yet complete, since there are a number of promising lines, of either theoretical or practical interest, not yet fully explored. Since, however, the further study of these has had to be deferred for the time being, it has been decided to record here the progress made so far.

EXPERIMENTAL

The shellac used for most of the experiments was a pure TN shellac, free from rosin and orpiment.

METHODS EMPLOYED

Mixing.—This was carried out on a laboratory mixing mill having rolls 12 × 6″ diam., revolving at 20 and 30 r.p.m., respectively, and heated to 50–55° C before commencing each mixing operation. The mixing time was adjusted to the size of the batch and the proportion of fillers according to the R.A.B.R.M. standard procedure.

Plasticity.—This was measured by the parallel-plate (Williams) plastometer, in which cylindrical specimens of constant volume, either 1.0 or 2.0 cc., are compressed endwise between parallel plates by a load of 5 kg., usually at an elevated temperature. The result is expressed as the thickness of the specimen after compression; complete time/thickness curves were obtained in every case, but are not always reproduced here.

Recovery.—A specimen of 14 mm. diameter and 13 mm. high, dusted with French chalk, was compressed in a parallel-plate plastometer fitted with distance pieces to determine the compressed thickness (this value is given in quoting the results). It was kept compressed for 5 seconds, then released, and its height measured periodically during recovery at the test temperature. Recovery is expressed as percentage of the amount by which the height was reduced by compression; readings of 0 and 100 thus represent perfectly plastic and elastic materials, respectively.

Scorching.—Strips of unvulcanized stock were heated for various periods at 105° C, cooled, and immersed in benzene for 1 hour, with occasional shaking. Scorching is indicated by the failure of the stock to dissolve and render the liquid cloudy or opaque. "Scorching time" is the heating period required to produce scorching.

Vulcanization.—This was carried out in moulds in a platen press, giving sheets either 5 mm. thick (for ring tensile specimens) or 2.5 mm. thick (for dumb-bells). From each mix 5 sheets were vulcanized for different periods, so that the "optimum" period, *i.e.*, that giving the best physical properties, could be determined by the method already described[6].

Tensile properties (tensile strength, elongation at break, elongation at constant load, modulus).—The technique used was substantially that of the British Standard Methods[7], using as specimens either the standard (Schopper) ring, or the dumb-bell of Type B.

Permanent set.—The permanent set, *i.e.*, residual extension after subjection to a relatively high elongation, was measured by the British Standard Method[7], except that the stretch and recovery periods were 15 and 60 minutes, respectively. The elongation used is stated in each case.

Hardness.—This was measured as the "hardness number," *i.e.*, the depth of indentation (mm/100) produced by a $\frac{1}{4}$"-diameter steel ball under a load of 1 kg., acting for 30 seconds. The result is substantially the same as the recently introduced British Standard Hardness Number[7].

Abrasion.—(1) *Akron-Croydon Machine.*—A disc of the rubber is rotated with its edge pressed against that of a freely-rotating abrasive wheel by a constant force. The planes of the disc and wheel are inclined at an angle of 15° to one another, the line of intersection passing through the centers of the disc and wheel[8]. Abrasion loss is expressed as cc. per 1,000 revolutions of the abrasive wheel. (2) *Du Pont Machine.*—Two rectangular rubber specimens are pressed by a constant force against a rotating disc of standard emery paper. Abrasion loss is expressed (1) as cc. per hour, (2) as cc. per h.p. hour of energy used in dragging the specimens over the abrasive surface[9].

Flexing.—Tests were made on the De Mattia machine, in which a moulded rubber strip, with a central transverse groove, is flexed 300 times per minute so that a relatively sharp bend occurs at the groove, causing cracking to develop there[10]. The results were examined by the method of Newton[11], giving finally the "flexing life", *i.e.*, the number of flexings required to produce a standard degree of cracking; since such experimental results have little absolute significance, they are given only as relative values.

Swelling.—The specimens were discs of 16 mm. diameter and either 2.5 or 5 mm. thick (thickness does not influence the results). The specimens were immersed in the swelling liquid at 25° C, and weighed periodically, the volume of liquid absorbed being deduced from the increase in weight.

Swelling results have been calculated by two methods:—(1) as volumes of liquid absorbed by 100 volumes of the vulcanizate this being the figure of direct practical interest, and (2) as volumes of liquid absorbed by 100 volumes of the rubber phase, *i.e.*, excluding the shellac and fillers, this being used to indicate the degree of vulcanization, because the more fully the rubber is vulcanized the less liquid it absorbs.

The swelling liquids were benzene (A.R.) and petroleum ether (b.p. 60–80° C).

Water absorption.—(1) *Immersion method.*—The method was similar to that for swelling, except that the specimens were 44 mm. in diameter, and different temperatures (as noted in the tabulated results) were used. Owing to the extreme slowness of water absorption, practicable test periods cover only the initial stages, during which absorption (A) is approximately proportional to the square root of the time of immersion (t); results are therefore expressed as $A/\sqrt{t}$.

(2) *Vapor method.*—The rubber, rasped to a fine crumb, is exposed to air of high relative humidity (as noted in the appropriate tables) until equilibrium absorption is attained, which requires only about 1 day[12].

Cross-breaking strength and elongation (*ebonite*).—Specimens 25 mm. wide and 5 mm. thick were broken by the normal 3-point loading method, using supports 51 mm. apart. Cross-breaking strength and elongation are the stress and strain respectively at the most-stressed part of the specimen at the moment of rupture, calculated from the breaking load and the deflection of the center of the specimen by the conventional formulas for the bending of a beam.

Impact strength (*ebonite*).—This was measured by the falling-weight machine, which delivers a vertical blow to the center of a horizontal bar-shaped specimen supported near its ends. Both unnotched and notched specimens were ex-

amined.   Details of the machine, specimens, and technique ("Method 2") are given by Church and Daynes[13].

Plastic yield (ebonite).—This was measured by the R.A.B.R.M. torsion method.   One end of a specimen 75 mm. long and 15 × 5 mm. cross-section is fixed, and the other end subjected to a torque of 75 g.-cm. applied for 30 minutes; the resulting twist (degrees) is taken as the "yield".   The test is repeated at various temperatures to give a temperature of yield curve[14].   With the shellac ebonites, however, the form of this curve did not permit the "yield temperature" to be deduced in the conventional manner.

I. MIXING SHELLAC INTO RUBBER

Shellac can be easily incorporated into rubber by the usual process of mixing on heated rollers, since at the normal temperature of the rubber during this process (80–90° C) shellac softens or melts and so disperses readily.   Mixtures containing up to 65 per cent of shellac can easily be obtained, and even 75 per cent can be reached with care.

Hard lac resin (acetone-urea process) has been found more difficult to disperse, because, if used in lump form, it does not break down or melt, and if used in powdered form, it tends to soften just enough to agglomerate into small lumps which do not redisperse.

Although shellac is easily incorporated and dispersed, it is not truly miscible with rubber, as the following observations show: (1) treatment of a rubber-shellac mixture with petroleum ether dissolves out the rubber, leaving a residue of shellac particles, which are elongated as a result of the passage of the mixture between the mill rolls, *e.g.*, in one case examined the particles were 5 to 15μ long and 1 to 2μ in diameter; this incidentally shows the degree of dispersion of the shellac; (2) a rubber-shellac mixture is normally transparent, since the two components have the same refractive index (1.52), but on stretching it becomes opaque and whitish, indicating the formation of vacuoles (as occurs with rubbers containing certain coarse fillers) and hence of discrete particles of shellac.   The latter observation suggests that rubber does not adhere very firmly to the surface of the shellac particles.

II. UNVULCANIZED RUBBER–SHELLAC MIXTURES.
GENERAL PROPERTIES AND POSSIBLE USES

The detailed study of these mixtures is described in the following section, concerned primarily with those properties of technical importance in rubber manufacture.   However, certain general observations that have suggested practical applications of the mixtures in the unvulcanized state may be noted here.

As would be expected, the addition of large amounts of shellac (40–100 parts per 100 of rubber) renders the rubber much stiffer and more thermoplastic, and when the two components are present in about equal amounts, the mixtures bear an outward resemblance to gutta-percha.   As both rubber and shellac have good electrical properties, this observation suggested the use of such mixtures to replace gutta-percha as an insulant or for other purposes, and indeed for various applications where a thermo-plastic material is required.

Two recent patents[15] relate to unvulcanized mixture of rubber, shellac, and mineral ingredients, although these are formed from aqueous dispersions, not by the dry mixing process described above; they are used for golf-ball covers and cable insulation respectively.   Apart from the latter patent and a few
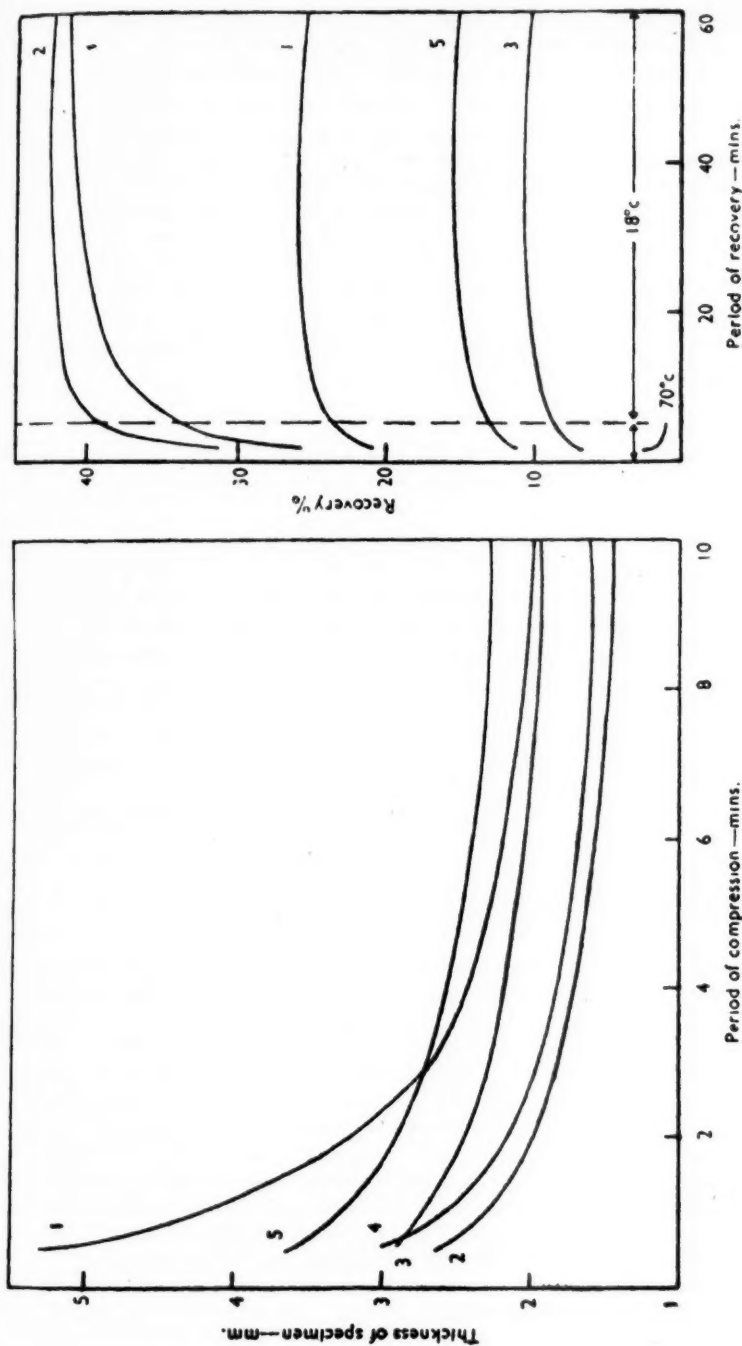
FIG. 1.—Plasticity and Recovery of unvulcanized rubber-shellac mixtures in comparison with gutta-percha. (1) Plasticity test, using 2 cc. specimens at 70° C. (2) Recovery test at 70° C. Compressed thickness = 4.8 mm.; Curve 1 and Curve 2: Deresinated gutta-percha, Samples 1 and 2; 3, Gutta-percha +50 per cent rosin content; 4, smoked sheet 50 per cent + T.N. Shellac 50 per cent; 5, smoked sheet 36 per cent + T.N. Shellac 27 per cent + amorphous silica 27 per cent + paraffin wax 10 per cent.

early ones[16], the possibilities of thermoplastic rubber-shellac mixtures for electrical purposes seem to have received little attention.

A few preliminary experiments have been made with mixtures of raw rubber (usually washed smoked sheet) and TN or dewaxed shellac, in some cases + a mineral filler (precipitated silica) and paraffin wax. Measurements of plasticity and of elastic recovery after deformation showed that some of these mixtures had much the same thermoplastic character as pure (deresinated) gutta-percha, while others more nearly resembled the crude gutta (Figure 1). The rubber-TN shellac mixture was superior to crude gutta, but inferior to pure gutta in resistance to water absorption; the latter, of course, is well known to be exceptionally resistant to water. A marked improvement was effected by substituting deproteinized rubber for smoked sheet and dewaxed for TN shellac. Typical, absorption figures, relating to specimens 2.5 mm. thick immersed in distilled water at 25° C, are as follows:

	Water absorption
	$(A/\sqrt{t})$
Deresinated gutta-percha	0.11
Deproteinized rubber (50 per cent) + dewaxed shellac (50 per cent)	0.27
Smoked sheet (50 per cent) + TN shellac (50 per cent)	0.60
Crude gutta-percha (50 per cent)	1.0

The silica used in the mixture referred to in Figure 1 was found to increase the absorption considerably.

Interesting results have been obtained also with rubber-shellac mixtures as adhesives for plywood, and a patent has been filed for their use in this way[17]. The glues commonly used for making plywood are affected by moisture and are very susceptible to attack by moulds and the like. Shellac is not so affected, but is comparatively brittle. However, rubber-shellac mixtures form thermoplastic adhesives which give plywoods with greatly improved resistance to impact. This is illustrated by the following test results, obtained by separating the plies by a blow normal to the surface:

Adhesive	Impact strength (kg.-cm. per sq. cm.)
Shellac alone	0.12
Shellac 75 per cent rubber 25 per cent	0.28
Shellac 67 per cent, rubber 33 per cent	0.34
Shellac 55 per cent, rubber 45 per cent	1.16

The lengthwise shrinkage produced by heating a calendered sheet of a rubber-shellac mixture (see "Grain effect", below) might be utilized in cases where it is desired to apply a wrapping or covering that is to be subsequently shrunk into close contact with the underlying surface. The shrinking effect could, of course, be enhanced by deliberately stretching the sheet while hot.

It is considered that the possibilities of unvulcanized mixtures of rubber and shellac, with or without other ingredients, as thermoplastic moulding materials, adhesives, binders for fibrous materials, impregnating agents, etc., deserve thorough investigation. A valuable feature of such mixtures is the wide range of physical properties obtainable by varying the proportions of rubber and shellac. Thermosetting mixtures could be made by adding vulcanizing agents for the rubber and catalysts for thermal hardening of the shellac.

Although patents exist for rubber-shellac mixtures, these would appear to have resulted largely from "hit and miss" trials. No systematic study of their properties seems to have been made, so that it cannot be said that their possibilities have been properly explored.

III. UNVULCANIZED RUBBER–SHELLAC MIXTURES. PROPERTIES OF IMPORTANCE IN RUBBER MANUFACTURE

(1) *Grain effect.*—When a rubber-shellac mixture is sheeted by passage between rolls and then quickly cooled, the resulting sheet possesses a marked anisotropy or grain effect, which is shown in the following ways:

(*a*) On heating, the sheet shrinks lengthwise and becomes thicker, to a greater extent the more shellac is present. Table I gives typical results for sheets heated at 70° C and at 90° C.

TABLE I

SHRINKAGE DUE TO GRAIN

Parts shellac per 100 rubber*	Decrease in length (percentage)		Increase in thickness (percentage)		Change in width (percentage)	
	70° C	90° C	70° C	90° C	70° C	90° C
0	12	10	7	6	+4	+4
2	12	11	12	7	+3	+3
5	17	13	10	8	+7	+5
15	22	25	15	23	+7	+7
40	22	39	23	35	+6	+5
100	25	44	38	85	−1	−6

* 3 parts of sulfur was added because it is necessarily present in all normal mixes.

(*b*) The sheet can be torn relatively easily along its length, but not so easily across. This difference is very pronounced when a fairly large proportion of shellac is present. Similar differences in resistance to tear have been observed by Kirchhof[18] in stretched films prepared by evaporating latex containing ammoniacal shellac solution.

Rubber mixings containing any considerable amount of shellac would, therefore, presumably have to be handled with the same precautions as those containing anisotropic mineral fillers, such as china clay and magnesium carbonate, to minimize undesirable shrinkage effects due to calender grain.

The effect of shellac in increasing grain is evidently due to its particles becoming elongated when the stock is passed between the mill rolls, as noted above. On cooling, the particles quickly harden and so prevent retraction of the strained rubber. Heating softens the shellac, and thus makes possible retraction.

It is important to note, however, that shellac does not produce grain in vulcanized rubber, presumably because, at the high temperature of vulcanization, both shellac and rubber are relatively fluid, and surface tension causes the shellac droplets to assume a more or less spherical form.

(2) *Plasticity.*—Substances that soften or plasticize raw rubber and unvulcanized stocks are important for two reasons: (*a*) raw rubber must be plasticized before fillers, etc., can be mixed with it; (*b*) when large amounts of such materials are incorporated, softeners must be added to make the stock suitable for calendering, extruding and moulding. Any substance which, like shellac, is very soft or fluid at processing temperatures (80–100° C) has some physical softening effect, and many well-known softeners act simply in this way. However for the initial plasticizing referred to in (*a*) much greater activity is shown by "peptizing agents," which, when used in quite small amounts, assist the disaggregation of the rubber apparently by promoting oxidation. It is, therefore, important to know whether shellac shows this chemical softening action, which is acquiring great technical importance.
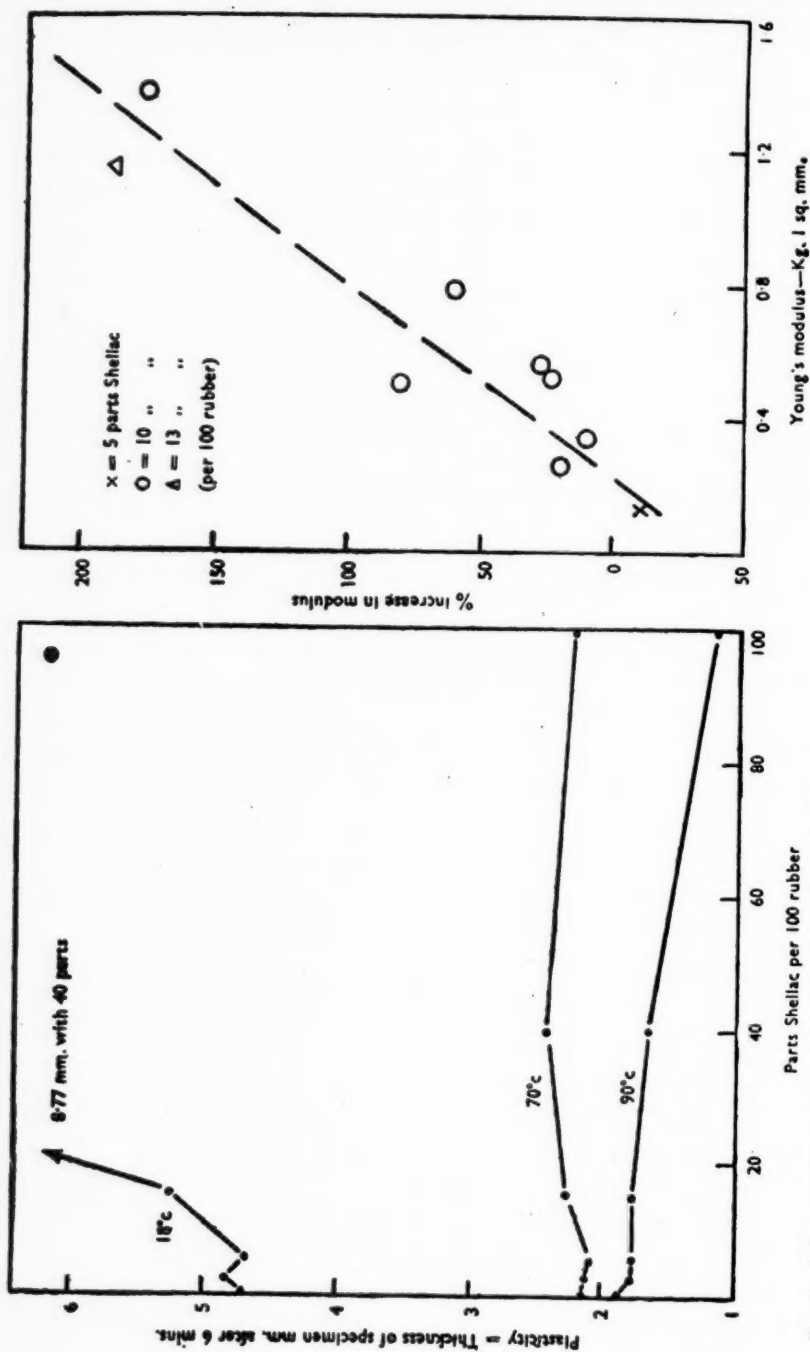
Fig. 3.—Effect of shellac on Young's modulus of vulcanized rubber in relation to the modulus of the blank mix.

x = 5 parts Shellac
O = 10 " "
△ = 13 " "
(per 100 rubber)

Young's modulus—Kg. 1 sq. mm.

% increase in modulus

Fig. 2.—Influence of increasing proportions of shellac on the plasticity of unvulcanized rubber at various temperatures.

Parts Shellac per 100 rubber

Plasticity = Thickness of specimen mm. after 6 mins.

8·77 mm. with 40 parts

18°c

70°c

90°c

To examine the effect of shellac on the softness or plasticity of rubber, various proportions of TN shellac were milled into a 100:3 mixture of rubber and sulfur. Results of plasticity tests are shown in Figure 2 for various temperatures.

At all three temperatures, amounts of shellac up to 5 parts have practically no effect. According to the plasticity test, therefore, shellac does not act as a peptizing agent. At 18° C, larger amounts stiffen the mixture, while at 90° C they soften it; at 70° C there is only a slight stiffening. The physical softening effect is thus shown only at or above about 90° C and only when relatively large amounts of shellac are used.

The way in which the effect of shellac varies with temperature is in keeping with the fact that at normal temperatures shellac is a hard solid, at 70° C a fairly soft plastic mass, and at 90° C a viscous liquid.

These results show also that shellac does not possess the property, shown by certain organic substances, e.g., benzidine and p-aminophenol, of stiffening unvulcanized stocks when added in small proportions, and thus helping extruded tubing, for instance, to keep its shape during processing. This conclusion was confirmed by direct tests of the deformation of the unvulcanized stocks under their own weight at 18° C.

(3) *Solution viscosity.*—The viscosity of a solution of rubber can likewise be used to indicate the degree of breakdown or peptization which it has undergone during milling. Benzene solutions of the stocks described above, and of such concentrations as to contain in each case 3 per cent of rubber, gave the following viscosities at 25° C:

Shellac (parts per 100 rubber)	0	2	5	15
Viscosity (centipoises)	12.8 ·	12.9	12.7	12.9

These results confirm the plasticity tests in showing that shellac has not peptized or assisted the breakdown of the rubber.

The stock containing 40 and 100 parts of shellac per 100 of rubber would not dissolve satisfactorily in benzene, lumps being still present after long standing and shaking.

(4) *Elastic recovery.*—The elastic recovery of unvulcanized rubber after deformation is important in relation to processing, because it causes an increase in the diameter of extruded materials on leaving the die of the extruder, and in the thickness of sheets leaving the nip between calender rolls, thus making it difficult to work to predetermined dimensions.

To see whether shellac markedly affects the elasticity, tests of elastic recovery were made on the same stocks as described above (Table II).

TABLE II

RECOVERY PERCENTAGE AFTER 1 HOUR

Temperature (° C) Compressed thickness	18 5.7 mm.	70 3.1 mm.	90 3.1 mm.
Parts shellac per 100 rubber:			
0	62	14	13.5
2	65	12	12
5	65	12	11
15	59	13	11.5
40	*	20	19.5
100	*	22	26.5

* Too stiff to be compressed to the thickness stated.

FIG. 3.—Effect of shellac on Young's modulus of vulcanized rubber in relation to the modulus of the blank mix. ... plasticity of unvulcanized rubber at various temperatures.

Only the two largest proportions of shellac, which are not likely to be used in normal mixes, have any marked effect, so that there appears to be little risk of difficulties arising from increased elastic recovery.

(5) *Scorching.*—Modern production methods demand the use of rubber stocks that are not likely to "scorch" or vulcanize prematurely during storage or in processing at elevated temperatures.

The effect of shellac has not yet been fully studied, but in no case has it been found to promote the scorching of stocks containing organic accelerators, indeed, there is somtimes a retarding effect, as was shown by tests on mixes containing rubber 100, sulfur 2, zinc oxide 5, titanium dioxide 5, whiting 100, stearic acid 2, mineral oil 1, tetramethylthiuram disulfide 0.25. The scorching times at 100° C were:

Shellac added	Scorching time (min.)
0	25
10 parts (TN)	80
10 parts (dewaxed lemon)	80
10 parts (TN) + 1 part MgO	80

This large effect is due not simply to the vulcanization process as a whole being retarded, since the period required to reach optimum vulcanization was increased only by some 20–40 per cent.

If such an effect on scorching were commonly found, shellac might attain extensive use as an antiscorching agent.

IV. INFLUENCE OF SHELLAC ON VULCANIZATION

Ordinary shellac interferes in some degree with the vulcanization of rubber by sulfur or a thiuram disulfide, though not always to an extent that would be serious in technical practice. This interference is not merely a retardation that can be counteracted by prolonging the vulcanization, because in all the experiments that demonstrate the interference, each mix has been vulcanized long enough to reach the optimum mechanical properties attainable with the mix in question.

The interference is shown in the following ways:—(1) In the presence of shellac there is more free sulfur and, therefore, less sulfur combined with the rubber. This is shown by the increased tendency of the vulcanizate to develop sulfur "bloom" (Table III) and also by analyses:

Mix	Free S. (percentage)
Rubber 100, sulfur 5	0.68
Do. + TN shellac 5	1.54

(2) The swelling, that is, the amount of a hydrocarbon liquid (benzene or petroleum ether) absorbed by the rubber-sulfur compound is increased, indicating a lower degree of vulcanization (fillers normally have the opposite effect on swelling). This is especially marked in vulcanizates made with certain organic accelerators, notably butyraldehydeaniline (BA) (Table XIV).

(3) In mixes containing organic accelerators, but free from fillers, the vulcanizate is rendered weaker, softer, and more stretchy and attainment of optimum vulcanization is retarded (Table VI).

Causes of interference.—The effect appears to arise, partly at least, from the acidic nature of shellac, because (a) it is most pronounced in presence of basic accelerators, such as diphenylguanidine (DPG) and butyraldehydeaniline

(BA) (Tables VI, IX, X, XII); (*b*) other acidic substances, *e.g.*, oxalic, benzoic, and stearic acids, similarly affect the properties of the vulcanizate; (*c*) addition of basic substances lessens the effect. Hydroxyl groups also seem to be a contributory factor, since acetylation of shellac has been observed to produce an improvement (Table IV), and certain hydroxy acids, *e.g.*, salicylic, produce a particularly strong interference.

It has not yet, however, been possible to explain why shellac has a stronger effect than other acids (oxalic, benzoic, stearic, and tartaric) used in such quantities as to contain the same, or even larger, amounts of the supposedly harmful groups.

Methods of overcoming interference.—Although improvement can be effected by using more sulfur, this is not a technically satisfactory procedure, as it leads to inferior aging properties and an increased tendency to develop sulfur bloom.

Sulfur bloom: A, trace; B, heavy; E, trace; F, slight.

More promising results have been obtained by neutralizing or reducing the acidity of the shellac. Addition of basic substances to the rubber mix is an obvious expedient, and experiments were made on these lines, using the base mix quoted above (Table III); butyraldehydeaniline was used because it is

TABLE III

Base Mix: Rubber 100, sulfur 2.5, zinc oxide 5, stearic acid 1, butyraldehydeaniline 0.75; tensile tests on ring specimens; hardness measured on specimens 10 mm. thick.

Mix	TN Shellac	MgO	Vulc.*	TS†	EB‡	E50§	H¶	PS‖ 400	Swelling** B	Swelling** PE
A	0	0	30/141	3100	740	505	128	213	370	212
B	5	0	95/141	1850	825	640	165	2.8	615	332
E	0	0.5	20/141	2650	755	550	135	2.5	430	229
F	5	0.5	50/141	2400	750	540	139	3.1	470	249

* Vulc. = optimum vulcanizing period and vulcanizing temperature; thus 15/153 denotes that the optimum is reached in 15 minutes at 153° C.
† TS = Tensile strength (lbs. per sq. in.).
‡ EB = elongation at break (percentage).
§ E 50 = elongation (percentage) under a load of 50 kg. per sq. cm. (710 lbs. per sq. in.).
¶ H = hardness number (Note that a high value denotes a soft rubber and *vice versa*).
‖ PS 100, 200, 400 = permanent set (percentage) after stretching to 100 per cent, 200 per cent, 400 per cent elongation.
** Swelling calculated on rubber, Method (b); B—Benzene; PE—petroleum ether.

the most adversely affected of the common accelerators by shellac. All the basic substances examined, magnesium oxide, adldehydeammonia, light (basic) magnesium carbonate, aniline, litharge, and borax, produced some improvement, the effect decreasing in the order named. The efficiency of magnesium oxide is illustrated by the data in Table III.

The figures for optimum vulcanizing period tensile strength, elongation at constant load, hardness, and swelling, and the observations on bloom, all show that magnesium oxide considerably lessens, though it does not eliminate, the harmful effects of shellac. It may be added that the addition of magnesium oxide did not spoil the aging properties (see also Table XIII).

It should be possible also to render the active groups in shellac harmless by suitable chemical modification of the molecule. The results in Table IV for various types and derivatives of lac give some idea of the possibilities in this direction, which, however, have not been fully explored; column 2 gives the acid values of the materials used.

Some of the modified lacs, especially those with reduced acid value, give much better results than TN or seedlac; moreover, the behavior of product Z5 is further improved by addition of magnesium oxide. The fact that sulfurized

TABLE IV

Base Mix: Rubber 100, sulfur 2.5, zinc oxide 5, stearic acid 1, butyraldehydeaniline 0.75
5 parts of shellac, etc., added; tensile tests on rings; hardness
measured on specimens 10 mm. thick.

Type of Shellac, etc.	Acid value	Vulc.	TS	EB	E50	H	PS 400	Swelling benzene (g)
(None)	..	35/41	3050	742	506	131	2.0	366
TN	72	95	2030	823	612	164	2.5	485
Seedlac	71	>100	1870	785	605	153	2.5	465
Sulfurized (a)	66	95	2000	790	595	158	2.2	463
Dewaxed (b)	68	90	2400	820	592	145	1.8	453
Z5 (c)	57	55	2520	785	543	141	3.2	..
Do. + 0.5 part MgO	..	60	2900	760	503	132	3.5	..
Do. + 2 parts MgO	..	45	2950	755	507	127	3.4	..
Acetylated (d)	91	75	2550	755	530	138	2.9	428
Hard lac resin (e)	61	50	2200*	710*	527	134	5.0	402
Shellac-drying oil compound	48	45	2870	765	535	132	5.1	406
Z4 (f)	13.5	50	2750	740	513	130	2.8	..

* Probably low, owing to poor dispersion of the lac resin.
 (a) Treated with 4 per cent sulfur at high temperature. (b) Solvent process, type DL. (c) Lac modified by treatment with linseed oil fat acids (84 per cent) and a monoglyceride (18 per cent). (d) Partially acetylated shellac. (e) Acetone-urea process. (f) Lac modified by treatment with stearic acid (112 per cent) and a mono-glyceride (53 per cent). (g) Swelling calculated on rubber (Method (b)).

lac is no better than the untreated material disposes of the view at one time
held that interference is due to the shellac taking up some of the sulfur.

As already noted, acetylated lac, although of high acid value, gives relatively
good results, suggesting that the hydroxyl groups in shellac are harmful.

It seems clear from these results that, if interference with vulcanization
were found to be a serious hindrance to the adoption of shellac as a rubber
compounding ingredient, modified lacs could be produced relatively, if not
entirely, free from this drawback.

V. INFLUENCE OF SHELLAC ON THE PROPERTIES OF THE VULCANIZATE

(1) *Mechanical properties: "pure" mixings.*—To show the effects of shellac
most clearly, experiments were first made on mixings containing only rubber
and the essential vulcanizing agent—sulfur. A second series was prepared with
a different vulcanizing agent—tetramethylthiuram disulfide (TMT) and the
necessary activators (Table V).

TABLE V

Rubber-sulfur base mix: Rubber 100, sulfur 5, tensile tests on rings; TMT base mix:
Rubber 100, TMT 2.5, zinc oxide 5, stearic acid 1; tensile tests on dumb-bells;
all hardness measurements on specimens 10 mm. thick.

Base mix	TN Shellac	Vulc.	TS	EB	E50	H	PS 400	Resilience*
Rubber-sulfur	0	165/153	1650	965	812	168	2.5	40
	5	160	1400	875	732	171	2.8	42
	15	150	1600	775	593	158	3.7	40
	40	140	1430	625	455	141	6.6	40
TMT	0	35/141	2150	730	620	153	3.2	..
	5	35	2150	680	540	140	6.4	..
	15	40	2370	650	450	131	11.0	..
	40	30	1800	580	375	128	..	..
	100	30	800	370	350	81	..	..

* Measured by Scleroscope; resilience = height of rebound of a steel striker allowed to fall from a height of 100 units.

Rate of vulcanization is not much affected by shellac in either series.

In the rubber-sulfur mix the only effects of shellac on the physical properties are a reduction in breaking elongation and a stiffening as shown by the E50 figures, and, when used in the larger amounts (15–40 parts), a slight hardening and an increase in permanent set. The fact that the resilience is maintained is an interesting feature, because fillers generally lower this property.

In the TMT mix much the same effects are observed, but the hardening and increase in permanent set are greater, and the strength is considerably lowered by the largest proportion of shellac.

It must be noted that in both series of mixes the hardening effect of shellac is relatively small, being less than that of even the so-called inert fillers. This is consistent with the fact that the particles of shellac in mixtures with rubber are relatively large (see Section I).

Accelerated mixes.—Attention was next turned to mixings of a more common type, that is, containing organic accelerators. Several different types of these were tried (Table VI).

TABLE VI

Base mix: Rubber 100, zinc oxide 5, stearic acid 1. Upper and lower lines of figures, for each accelerator, refer respectively to mixings without and with 5 parts TN shellac. Tensile tests on rings; hardness measured in specimens 10 mm. thick.

Accelerator	Sulfur	Vulc.	TS	EB	E50	H	PS 400
Mercaptobenzothiazole (MBT)	2.5	38/141	1900	818	657	160	3.0
0.75		55	1650	812	648	168	3.5
Vulcafor DAU, 0.375	2.0	25/135	2400	815	570	137	2.5
		35	2180	793	550	142	3.0
Zinc pentamethylenedithiocarba-	2.0	28/126	2600	794	587	138	3.0
mate (ZPD) 0.35		35	2300	783	567	142	3.9
Zinc diethyldithiocarbamate	2.0	18/126	2670	806	543	132	2.9
(DC) 0.4		20	2430	797	524	134	3.0
Hexamethylenetetramine (HMT)	3.0	48/153	1970	761	600	147	2.7
0.75		55	1670	752	599	152	3.2
Diphenylguanidine (DPG) 0.75	3.0	30/153	2310	721	540	136	2.5
		35	1630	757	599	155	3.4
Zinc α-phenylbiguanide (ZPB)	2.5	43/153	1950	832	640	148	2.8
0.75		50	430	765	..	207	10.0
Butyraldehydeaniline (BA) 0.75	2.5	30/141	2930	718	499	129	2.6
		100	1850	802	620	162	3.2
Tetraethylthiuram disulfide	2.0	40/126	2230	795	617	147	2.8
(TET) 0.25		>40*	1630	788	633	164	5.0
Zinc isopropylxanthate (ZIX) 1.0	2.5	25/108	2500	743	552	138	3.0
		33	1600	796	635	171	6.8
Lead dimethyldithiocarbamate	3.0	15/153	2800	482	681	127	4.5
(LDC) 0.75†		15	3050	446	670	121	7.2

* Did not reach optimum vulcanization at the longest time given; properties quoted are for the 40-minute vulcanizate.

† As this accelerator requires litharge for activation, 14 parts were used in place of 5 parts zinc oxide.

With the first five accelerators in the Table, shellac makes the product slightly less extensible, as judged by E50, though softer according to the hardness test; tensile strength is reduced and permanent set is increased.

With the next five (DPG–ZYX) the softening, lowering of tensile strength, and increase of permanent set are more pronounced, and the rubber is now rendered more extensible.

The changes produced by shellac in the various mechanical properties arrange the accelerators in much the same order of merit, the average being as follows:

Least affected by shellac: LDC; ZDC; ZPD; Vulcafor DAU; MBT, HNT; TET; DPG; ZIX; BA; and most affected: ZPB.

It may be said that, with the first six accelerators in this list, shellac does not seriously affect the properties of the vulcanizate; with ZIX and BA it is strongly detrimental, and with ZPB very strongly so, at least in the type of mix used in these tests. However, ZIX and ZPB are not extensively used in normal rubber mixes.

The retardation of vulcanization does not follow the same order, except that BA is again one of the most adversely affected, being in fact the only one seriously retarded.

The good results given by LDC can be ascribed, in part at least, to the beneficial effect of the litharge used to activate it (see Section IV). Although there is thus no evidence that LDC as such is superior to the other accelerators, it does appear to be one of those that are compatible with shellac.

It is significant that the three accelerators which give the best results in the presence of shellac (LDC, ZDC, ZPD) are all metallic salts of dithiocarbamic acids. The results also give some confirmation of the statement[19] that acidic accelerators give better results than basic ones.

Conclusion.—Taking the above results as a whole, it cannot be said that they indicate any improvement in the properties of the vulcanizate by addition of shellac, such as would suggest uses for it as a rubber compounding ingredient.

It must, however, be particularly noted that this conclusion applies only to mixings of the "pure" type, *i.e.*, containing no mineral fillers, since more promising results have been obtained with mixings containing such materials.

(2) *Mechanical properties: mixings containing fillers.*—Tests were next made with various mixings containing relatively large proportions of fillers:

Carbon black mix, as might be used for high grade soles and heels and other abrasion-resistant articles, and all rubber hose.

China clay mix, as used for flooring and tiling.

Whiting mix, as used, *e.g.*, for moulded hot-water bottles.

Mix containing a large proportion of reclaimed rubber; it is important to test the compatibility of shellac with the latter, as it is largely used in mechanical goods, hose, and cheap soles and heels.

(a) *Carbon black.*—The first series of mixes, using four different accelerators (Table VII), show that shellac never seriously retarded vulcanization, although

TABLE VII

Base mix: Rubber 100, gas black 75, zinc oxide 5, stearic acid 3, pine tar 4. Tensile tests on dumb-bells; hardness measured on specimens 5 mm. thick.

Accelerator	Sulfur	TN Shellac	Vulc.	TS	EB	M100	M300	H	PS 200
DPO, 1.2	3.0	0	28/153	3640	410	600	2680	29	12
		10	35	2850	390	775	2180	12	30
MBT, 1.2	2.5	0	35/148	3620	395	720	2650	25	12.5
		10	35	2990	360	935	2450	14	32
ZPD, 0.6	2.0	0	40/126	3710	415	690	2940	25	13
		10	55	3210	390	840	2590	11	28
TET, 0.4	2.0	0	35/126	3640	410	560	2880	23	9
		10	40	3150	410	775	2410	11	30

the tensile strength was somewhat lowered, to about the same extent with all four accelerators. The increase in permanent set seemed to be particularly large in this experiment.

The modulus figures are interesting because they show that shellac made the rubber stiffer at small extensions (M100) but less stiff at higher extensions (M300), indicating a change in the shape of the stress-strain curve. This probably arises from the poor adhesion between rubber and shellac (see Section I). The most striking manifestation of the effect of shellac on the stress-strain relationship is in the hardness, which is related to the modulus at very small strains. The fact that the hardness number is approximately halved by adding shellac means that this modulus is increased by nearly 200 per cent.

The hardening effect of shellac suggested an interesting application, namely, to enable very hard vulcanized products, such as soles, all-rubber hose, etc., to be obtained without using so great a proportion of carbon black. This would help the mixing and processing of the unvulcanized stock, because the reduction of the carbon black content and the addition of shellac would make it softer and more thermoplastic. Table VIII gives the results of tests made to try out this idea.

TABLE VIII

Base mix: Rubber 100, sulfur 2.5, zinc oxide 5, stearic acid 3, MBT 1.2; + the following:

Mix	Gas black	Pine tar	TN shellac	Magnesium oxide
A	40	3	0	0
B	40	3	7	0.7
C	40	3	15	1.5
D	60	4	0	0
E	60	4	7	0.7
F	60	4	15	1.5
G	90	6	0	0

Mix	Vulc.	TS	EB	M100*	M300	M500	H	PS 100	Abra-sion	Flex†	Pl‡
A	35/148	4310	635	260	1225	2940	51	2.3	0.21	100	91
B	28	3640	682	190	760	1940	45	3.3	0.37	110	90
C	25	3230	633	275	960	2210	37	3.5	0.45	140	91
D	35	3980	583	325	1510	3310	38	2.5	0.16	45	178
E	25	3240	605	300	1140	2540	30	4.6	0.22	50	224
F	25	2310	558	360	1210	2440	23	4.9	0.36	35	230
G	35	3140	398	725	2500	..	19	4.6	0.20	30	645

* M100, 300, 500 = modulus at 100 per cent, 300 per cent, 500 per cent elongation, *i.e.*, load (lbs. per sq. in.) required to produce the elongation.
† Flex = flexing life (relative values only).
‡ Pl = plasticity reading, *i.e.*, thickness of compressed specimen (mm./100): unless otherwise stated compression period is 6 min.
Tensile tests on dumb-bells; hardness measured on specimens 5 mm. thick; abrasion by Akron-Croydon machine; plasticity (Pl) measured at 90° C on 2-cc. specimens.

The fact that vulcanization is now quicker in the presence of shellac must be ascribed to the beneficial effect of the magnesium oxide added with it.

In practically every case the moduli with 7 parts shellac are lower than with 0 or 15 parts; this suggests that when the larger amount is used the physical stiffening effect of the shellac begins to neutralize the softening due to interference with vulcanization.

On the other hand, the rubber becomes progressively harder as the shellac content is increased, so that 40 parts black + 15 shellac (C) give the same hardness as 60 black and no shellac (D), and the mix with 60 black + 15 shellac (F) is nearly as hard as that with 90 black (G). The technical advantage of using the black-shellac combination is strikingly shown by the plasticity

figures, since C is softer than D, and F much softer than G. A study of the complete plasticity results shows that these stocks are plastic materials as defined by Bingham[20], so the flow properties can be defined in terms of fluidity and yield value, *i.e.*, the stress needed to cause flow to begin; the approximate values of these, relative to mix C as unity, are:

Mix	C	D	F	G
Fluidity	1.0	0.15	0.12	0.01
Yield value	1.0	10	20	300

In each case the use of shellac in place of part of the black increases the fluidity about tenfold and reduces the yield value to one-tenth or less. The shellac mixes C and F should, therefore, be much easier to mix, process, and mould than those without shellac.

This improvement is unfortunately accompanied by a loss of abrasion resistance in the finished product, as judged by the abrasion test figures in Table VIII (compare C with D, and F with G). This would be a disadvantage in rubbers where the best possible abrasion resistance is required, notably in tire treads.

On the other hand, there is evidence that resistance to flexing is improved. Thus the shellac mix C shows about three times the flexing life of the all-black mix D. As flexing resistance is very important in soles, tire side-walls, belt covers, and various other articles, the use of shellac might be advantageous in these cases.

(b) *China clay and whiting.*—With each of these fillers a series of mixings was first made analogous to those in Table VII, *i.e.*, using four different accelerators. Both TN shellac and dewaxed (solvent process, type DL) shellac were examined. As the results were in many respects similar to those for the carbon black mixings, they are given here only in summarized form.

Vulcanization was usually somewhat retarded by both types of shellac, the increase in optimum vulcanizing period averaging 23 per cent, but only once exceeding 30 per cent (DPG—china clay mix).

Table IX gives the tensile properties of each shellac mix as percentages of

TABLE IX

China clay base mix: Rubber 100, clay (Devolite) 200, zinc oxide 5, mineral oil 2, stearic acid 5, titanium dioxide 5. Whiting base mix: Rubber 100, whiting 100, zinc oxide 5, titanium dioxide 5, stearic acid 2, mineral oil 1.
Tensile tests on dumb-bells.

Filler	Accelerator		Sulfur	TN shellac, 10 pts.				Dewaxed shellac, 10 pts.			
				TS	M100	M500	PS	TS	M100	M500	PS
China clay	DPG	1.0	3.0	75	73	*	65	69	74	*	60
	MBT	1.0	2.5	87	121	*	100	84	126	*	110
	ZPD	0.5	2.0	83	111	*	78	89	116	*	75
	TET	0.35	2.0	77	117	*	90	78	125	*	75
Whiting	DPG	0.76	3.0	66	70	77	80	64	75	71	90
	MBT	0.75	2.5	80	120	100	75	80	130	98	110
	ZPD	0.4	2.0	84	110	107	90	85	105	108	100
	TET	0.45	2.0	74	104	90	107	75	127	96	85

* Broke below 500 per cent elongation.

those for the corresponding blank mix. Elongation at break is omitted because it showed throughout a uniform decrease of 5–10 per cent by addition of shellac.

The results resemble those for the gas black mixings in that the strength is lowered and the modulus at 100 per cent usually increased.   However, a striking feature not observed in any of the previous experiments is that the permanent set is usually reduced; this result has been found in tests with other china clay and whiting mixes.

Hardness figures, which are of greater interest, are given in Table X both as actual values and as percentage of the corresponding blank value.

TABLE X

(Mixings as in Table IX)

Filler	Accelerator	Hardness number			Percentage of blank	
		Blank mix	TN shellac	Dewaxed shellac	TN shellac	Dewaxed shellac
China clay	DPG	54	44	43	82	80
	MBT	51	34	34	67	67
	ZPD	53	33	36	62	68
	TET	54	32	30	59	56
Whiting	DPG	72	78	82	108	114
	MBT	75	68	71	91	95
	ZPD	72	67	65	93	90
	TET	73	64	64	88	88

In the clay mixes shellac always has a hardening effect, which is sometimes considerable.   With whiting, however, the effect is only slight, if present at all.

In both series of mixings shellac gives the least satisfactory results in presence of DPG; this is seen in the relatively low figures for tensile strength and modulus (Table IX) and high percentage figures for hardness.   The inferiority of DPG for shellac mixings agrees with the results in Table VI for pure mixings.

On the whole there is very little difference between TN and dewaxed shellacs.

As the hardening effect of shellac was again clearly evident with china clay, another series of clay mixings was made analogous to those in Table VIII, so as to examine further the possibility of using shellac to harden the vulcanizate without stiffening the unvulcanized stock.   Unfortunately, some of the mixings gave anomalous results, which it would be desirable to check if further work on the subject is undertaken, in particular, the flexing test results varied so irregularly from mix to mix that they gave no indication whether the improvement observed in the carbon black mixes was again present.   The other results are summarized in Table XI, the anomalous figures being given in brackets. It will be seen by comparing E and F with G that the use of shellac has again produced a much harder vulcanizate from a mix that is softer in the unvulcanized state.   In one respect, indeed, these results are more favorable than those obtained with carbon black, since the shellac mixings E and F are only little, if at all, inferior in abrasion resistance or tensile strength to either the corresponding mix without shellac (D) or the more heavily loaded stock (G). Moreover, the adverse effect of shellac on abrasion in the A–C series is much less than in the corresponding carbon black mixings in Table VIII.

The results obtained with china clay thus agree with those for carbon black in showing that shellac can be used to produce very hard vulcanizates without the disadvantage that would arise if an attempt were made to do this by incorporating larger amounts of filler.   In the clay mixings there is the additional

TABLE XI

Base mix: Rubber 100, sulfur 2, zinc oxide 5, titanium dioxide 5, stearic acid 2, ZPD 0.5; plus the following:

Mix	Clay (Devolite)	Mineral oil	Dewaxed lemon shellac	Magnesium oxide
A	200	5	0	0
B	200	5	10	1.0
C	200	5	20	2.0
D	250	6	0	0
E	250	6	10	1.0
F	250	6	20	2.0
G	300	7	0	0

Mix	Vulc.	TS	EB	M100	H	PS 100	Abrasion cc./hr.	Abrasion cc./hp.-hr.	Pl
A	28/126	1700	310	780	51	9.5	4.85	420	155
B	28	1400	330	615	42	7.5	5.05	460	136
C	35	950	320	470	40	11.0	6.0	495	156
D	35	1160	265	660	(64)	(21)	3.7	350	234
E	33	1040	275	630	34	11	3.7	355	162
F	40	970	240	725	23	9	3.9	385	159
G	30	1030	245	620	48	11	4.4	430	289

Tensile tests on dumb-bells; hardness measured on specimens 5 mm. thick; abrasion by Du Pont machine; plasticity (Pl) measured at 90° C using 1-cc. specimens.

advantage that incorporation of shellac does not appreciably impair the resistance to abrasion.

(c) *Reclaimed rubber.*—To test the compatibility of shellac with reclaimed rubber, a series of mixings containing a large proportion of the latter were made, using the same four accelerators as in the previous series (Table XII).

TABLE XII

Base mix: Rubber 40, whole-tire reclaim 100, zinc oxide 5, stearic acid 2. Tensile tests on dumb-bells: Hardness measured on specimens 5 mm. thick.

Accelerator	Sulfur	TN shellac	Vulc.	TS	EB	M100	M500	H	PS 200
DPG 1.0	3.0	0	23/153	2740	625	180	1730	85	4.5
		10	25	2520	600	205	1770	83	4.0
MBT 1.0	2.5	0	20/141	2890	625	170	2020	80	5.3
		10	40	2640	545	300	2190	73	4.8
ZPD 0.5	2.0	0	10/126	3240	680	155	1810	93	4.0
		10	33	2950	605	215	1940	77	—
TET 0.35	2.0	0	20/126	3020	625	175	1900	88	3.8
		10	33	2820	560	235	2210	73	4.0

The effect of shellac on the rate of vulcanization shows some new features, since DPG is not affected, whereas the other three accelerators are retarded. This is not surprising, for it is well known that organic accelerators do not behave in the same way with reclaim as with new rubber. The important point to note is that the mixes containing reclaim and shellac vulcanize at rates which are quite normal for the accelerators used (see Table VII).

The effects of shellac on the mechanical properties of the vulcanizate are of the same general nature as in the previously described mixings. It may be particularly noted that tensile strength is only slightly reduced and permanent set is not increased.

(d) *Conclusion.*—The most striking result shown by the tests on mixings containing fillers is the notable increase in hardness that may be produced by a small proportion of shellac, and which has been observed also in other experiments not described here.   Generally speaking, this increase is greater the harder the base mix to which the shellac is added.   This is illustrated by Figure 3, in which the hardening effect of shellac (usually 10 parts per 100 parts of rubber), expressed as the percentage increase in elastic (Young's) modulus, is plotted against the corresponding modulus of the base mix.

Such large increases in modulus as are produced in some cases can scarcely be ascribed simply to the fact that an extra amount of hard solid matter is being incorporated.   Thus, in the china clay mixings (Table XI) 10 parts of shellac have more hardening effect than an extra 100 parts of china clay.

It thus seems that the effect of shellac and a filler together is not merely the sum of the effects of the two used separately, but that there is some interaction, such as improved dispersion of the filler, or a finer dispersion of the shellac due to the presence of the filler particles.   It does not seem likely that the wetting of the filler is improved, in view of the poor adhesion between shellac and rubber.

A patent[3] published since these experiments were carried out claims a similar hardening effect in mixes containing mineral fillers, and states that it is due to reaction between the shellac and basic oxides present in the mix, forming brittle shellac salts.   According to the present experiments, however, in mixings without filler but containing 5 per cent zinc oxide, shellac has actually less hardening effect than the usual inert fillers, even when vulcanization is effected by a thiuram disulfide, which seems to be the least adversely affected by shellac (Table V).   Moreover, the use of alkali reclaim, which normally contains a little free alkali, does not cause shellac to have an unusually large hardening effect.   These results do not support the hypothesis stated in the patent; indeed it seems improbable that the shellac salts, merely because they are brittle, would have any more hardening effect on the rubber than shellac itself, since this is quite hard.

It is clear that this effect of shellac deserves further study, as it might well yield results of great value in connection with the use of shellac, as well as in relation to the study of dispersion and reinforcement.

(3) *Aging.*—Accelerated aging tests, mostly by the Geer oven method (air at 70° C), on several sets of mixings with and without various accelerators and fillers have all shown that shellac (TN or dewaxed) has no detrimental effect on aging.   On the other hand, there is no evidence in the Geer oven tests of any appreciable preservative effect, but in one series of experiments using the oxygen bomb test (70° C and 300 lbs. per sq. in. oxygen pressure) shellac seemed to produce a definite improvement (Table XIII).

TABLE XIII

Base mix: Rubber 100, sulfur 2, whiting 100, zinc oxide 5, titanium
dioxide 5, stearic acid 2, mineral oil 1, TET 0.25.

	Percentage fall in tensile strength	
Addition	48 hrs. in oxygen bomb	10 days in Geer oven
Nil	90	60
TN shellac, 10	50	52
Do. plus MgO, 1.0	32	54
Dewaxed lemon shellac, 10	24	45

(4) *Swelling in hydrocarbon liquids.*—Swelling tests were made on several of the vulcanizates already described to test the claims that have been made as to the beneficial effects of shellac in improving oil-resistance (see Table XIV).

It has been shown[21] that any factor which makes the vulcanizate harder reduces the swelling, and that the swelling in either benzene or petroleum ether is approximately proportional to the B.S. Hardness number, so that the ratio of swelling to hardness number (S/H ratio) tends to be constant, at least for fairly soft rubbers such as were used in the present tests. Any ingredient which markedly reduced this ratio would be useful in making oil-resisting rubbers, for which reason the S/H ratio is included in Table XIV.

TABLE XIV

Swelling (B = benzene; PE = petroleum ether)

Base mix	Shellac* etc., added	Swelling calculated on vulcanizate		Swelling calculated on rubber		S/H†	
		B	PE	B	PE	B	PE
Rubber 100, sulfur 5	0	500	258	500	258	2.97	1.53
(Table V)	5	528	282	549	293	3.08	1.65
	15	492	263	553	296	3.12	1.66
	40	470	249	620	330	3.33	1.76
Rubber 100, sulfur 5	0	479	..	479	..	2.87	..
	15	490	..	551	..	3.00	..
	15 + 1.0 sulfur	422	..	474	..	2.96	..
	13 + 2.0 sulfur	375	..	422	..	2.90	..
Do. 10 PbO	0	416	..	419	..	2.75	..
	15	389	..	443	..	2.97	..
BA Mix	0	370	212	370	212	2.95	1.67
(Table III)	5	595	320	613	332	3.6	1.93
	5 + 0.5 sulfur	520	275	536	285	3.4	1.80
	5 + 1.0 sulfur	480	262	595	272	3.2	1.76
Do. plus 0.5 MgO	0	430	229	430	229	3.2	1.70
(Table III)	5	455	238	470	249	3.5	1.72
TMT-vulcanized mix	0	450	292	450	292	2.95	1.91
(Table V)	5	447	285	460	296	3.18	2.02
	15	475	260	525	291	3.6	1.98
	40	553	246	700	323	4.3	1.93
	100	650	205	1100	365	8.0	2.5

* TN in all cases.
† S/H = ratio of swelling (calculated on the vulcanizate) to hardness number.

The following conclusions are indicated by these results:

(*a*) Addition of shellac alone does not in general markedly reduce the swelling, and never reduces the S/H ratio, but has rather the reverse effect. (Fillers in general do not increase this ratio[21]).

(*b*) The figures for swelling calculated on rubber show that the rubber phase in the shellac mix nearly always swells more than that in the blank, indicating a lower degree of vulcanization in the former, as already noted.

(*c*) By increasing the proportion of sulfur in the rubber-sulfur and BA mixes the swelling and S/H ratio are reduced, but the latter is not brought below the figure for the mix without shellac, so that no real advantage has been gained by adding shellac + extra sulfur.

It thus seems clear that in the type of mix examined, *i.e.*, free from mineral fillers, shellac is not better than the usual compounding ingredients in reducing

the swelling of vulcanized rubber in hydrocarbon liquids. This conclusion agrees with previous published work[22].

However, the investigation should be extended to mixings containing large proportions of filler, such as are commonly used as oil-resisting rubbers. Moreover, another important aspect of oil resistance remains to be examined, that is, the effect of shellac on the mechanical strength of the swollen rubber; the loss of strength due to swelling can be a more serious factor than the mere increase in volume, and it has been found that certain fillers are unexpectedly efficient in maintaining strength in the swollen rubber.

It may be added that shellac itself, after being heated under vulcanizing conditions, either alone or with sulfur, absorbs nearly its own volume of benzene but only a small amount (about 5 per cent) of petroleum ether.

(5) *Water Absorption.*—This was examined by both the vapor and immersion methods described.

TABLE XV

Water Absorption

Base mix	TN shellac	Vapor method*; equilibrium absorption	Immersion method $A/\sqrt{t}$
Rubber 100, sulfur 5	0	1.65	0.245
	5	1.75	0.26
	15	1.7	0.26
	40	1.9	0.23

* At 97 per cent relative humidity and 20° C; powdered TN shellac gave an absorption of 3.4 per cent under these conditions.

Neither method of test indicates much improvement from addition of TN shellac, a result which is not surprising in view of the fact that TN shellac itself absorbs more water than the rubber-sulfur vulcanizate.

A further set of experiments was made in view of a statement by a rubber manufacturer that vulcanized rubbers with exceptionally low water absorption were obtained by using shellac in combination with linseed oil, the shellac being simply "soaked" in the oil before adding the whole to the rubber mix. The mixes were of the type used, *e.g.*, for moulded hot-water bottles, and were made up from the following base stock:

Rubber 100, sulfur 2.0, zinc oxide 5, titanium dioxide 5, stearic acid 2, zinc diethyldithiocarbamate 0.4.

Two different fillers were used: whiting and blanc fixe, the latter being selected because it sometimes increases water absorption owing to the presence of traces of soluble salts, and might, therefore, be expected to bring out more clearly the beneficial effect of any water-repellent additions.

Results of immersion tests in water at 70° C on samples 2.5 mm. thick are given in Table XVI; vulcanizing periods of 20 and 30 min. at 126° C were used for each mix.

It is clear that neither the shellac-linseed oil mixture nor either of these materials separately has rendered the rubber more resistant to water absorption, the effect being generally in the opposite direction.

(6) *Color.*—TN shellac produces a pink discoloration when added to light-colored rubber stocks containing zinc oxide. The color persists after vulcan-

TABLE XVI

| Filler | Boiled linseed oil | Dewaxed lemon shellac | Absorption ($A/\sqrt{t}$) | |
			20 min. vulcanizate	30 min. vulcanizate
Whiting, 100	..	..	2.3	2.0
	6	..	3.3	2.9
	3	5	2.9	3.0
	..	10	2.9	2.7
Blanc fixe 150	..	..	3.1	2.8
	6	..	4.0	3.5
	3	5	4.1	3.5
	..	10	4.2	2.8

ization, and is apparently due to reaction of the natural lac dye with zinc oxide. In a white mix pigmented with 5 per cent of titanium dioxide, even 2 per cent of TN shellac produces a noticeable color, so this type of shellac would appear to be unsuitable for white or lightly colored vulcanizates.

Comparisons were accordingly made with other types of lac to see if this undesirable effect could be eliminated. A sample of seedlac (Kusum × Khair) gave a similar discoloration to TN shellac, though rather less pronounced. Hard lac resin (type T-5) was distinctly better, while dewaxed shellacs (dewaxed lemon, and solvent process type DL) and lac bleached with sodium hypochlorite were better still, giving only a slight gray or pinkish-gray discoloration. It is thus evident that the discoloring effect can be largely eliminated (see, however, Section VII in regard to the bleached lac).

VI. SHELLAC IN EBONITE

Some preliminary experiments have been made to see whether the incorporation of TN shellac or hard lac resin into a rubber-sulfur ebonite mix improves the mechanical or electrical properties of the product.

As one important object in compounding ebonite is the raising of the plastic yield temperature, the effect of various substances that accelerate the heat-hardening of shellac was tried (mixes C-G). All the mixes comprised rubber 65, sulfur 35, the following additions being made:

Mix K	(nil)
Mix B	40 pts. TN shellac.
Mix C	40 pts. TN shellac + 1.4 pts. phthalic anhydride.
Mix D	40 pts. TN shellac + 1.4 pts. hexamethylenetetramine.
Mix E	40 pts. TN shellac + 1.4 pts. lime (slaked).
Mix F	40 pts. TN shellac + 1.4 pts. piperidine.
Mix G	40 pts. TN shellac + 1.4 pts. ammonium oxalate.
Mix L	40 pts. TN shellac + 1 pt. magnesium oxide.
Mix M	40 pts. sulfurized lac (treated with 4 per cent sulfur).
Mix N	40 pts. sulfurized (treated with 4 per cent sulfur) lac + 1 part magnesium oxide.
Mix H	40 pts. hard lac resin (acetone-urea process).

All the mixes were vulcanized for 5 or 6 hours, at 155° C, which previous experience has shown to give a well-vulcanized ebonite from the blank (K) mix. As shellac seemed to retard vulcanization, this was in some cases extended to 8 hours. Mix D gave a porous product which was useless for test purposes. Results for the remaining mixes are summarized in Table XVII.

TABLE XVII

	Vulc.	K	B	C	E	F	G	L	M	N	H
Cross-breaking strength, kg. per sq. cm.	5	1295	635	560	460	485	475	..	..	..	695
Cross-breaking elongation (percentage)	5	11	5	4	4	4	5	..	..	..	4
Impact strength (kg.-cm. per sq. cm.)											
Unnotched	5	38	13	6	8	6	8	..	..	..	10
Notched	5	2.2	0.5	1.4	0.5	0.6	0.9	..	..	..	1.3
*Yield temperature (° C)	5	91	84	83	$84\frac{1}{2}$	$84\frac{1}{2}$	$86\frac{1}{2}$	81	$83\frac{1}{2}$	..	$84\frac{1}{2}$
	6	$91\frac{1}{2}$	84	..	..	..	..	84	86	85	..
	8	..	$87\frac{1}{2}$	..	..	..	..	$84\frac{1}{2}$	88	..	..
Permittivity:											
800 cycles per sec.	6	2.9	3.4	..	..	..	..	3.3	3.3	3.4	..
10^6 cycles per sec.	6	2.9	3.2	..	..	..	..	3.1	3.1	3.2	..
Power factor (percentage):											
800 cycles per sec.	6	0.49	0.78	..	..	..	..	0.77	0.68	0.81	..
10^6 cycles per sec.	6	0.88	2.2	..	..	..	..	2.3	2.1	2.3	..
†Water absorption (percentage)	5	1.4	3.4	2.8	2.8	2.1	1.8	..	..	..	1.4

* Temperature corresponding to a yield of 5° in the torsion test.
† Vapor method, at 98 per cent relative humidity at 25° C.

TABLE XVIII

	Vulc.	TS	EB	ESO	H	PS	*Swelling in benzene
No shellac	35/141	3050	742	506	131	2.0	366
Bleached shellac, 5	>100	1180	865	740	170	5.0	635

* Calculated on rubber, method (b).

These results indicate the following conclusions:

(a) Both TN shellac and hard-lac resin make the ebonite mechanically weaker, as judged by either a static (cross-breaking) or dynamic (impact) test.

(b) The lowering of the yield temperature shows that heat stability is somewhat reduced by all the shellac products; even after 8 hours' vulcanization, mixes B, L, and M have not reached quite so high a yield temperature as the blank (K) mix at 5 hours.

(c) The permittivity and power factor figures show that TN shellac and sulfurized lac increase the dielectric power loss of a rubber-sulfur ebonite. Results published by Karim[23] gave the very low power factor of 0.45 per cent for shellac, which might seem at variance with the present observation that shellac increases the power factor of ebonite, especially at high frequencies. Karim's tests, however, were apparently made at a frequency of only 50 cycles per second, so it would appear that the power factor of shellac increases rapidly with the frequency.

(d) TN shellac increases the water absorption, though to a less extent if a hardening agent is present; hard lac resin, however, does not do so.

From these preliminary results, therefore, shellac does not seem a promising ingredient for those types of ebonite where high mechanical strength and low dielectric power loss are essential. The work should, however, be extended to general-purpose ebonites where the demands are less exacting, and in particular to mixes containing fillers, where shellac might be expected to be helpful,

e.g., in facilitating mixing, processing, and moulding, and improving the surface finish.

VII. COMPARISON OF DIFFERENT TYPES OF LAC

Although most of the experiments have been made with TN shellac, several references are made above to tests with seedlac, dewaxed shellac, bleached shellac, sulfurized lac, and hard lac resin (see Sections IV, V(2), V(3), V(6) and VI and Tables IV, IX, X, XI, and XVII).

These show that seedlac and sulfurized lac behave in much the same way as TN shellac, and that dewaxed shellac sometimes gives rather better mechanical properties and always less discoloration. The hard lac resin (acetone-urea process) referred to in Table IV gave distinctly better results, apart from low tensile strength due to poor dispersion, but another type (T-5) did not appear better than ordinary shellac, except in producing less discoloration.

The sample of bleached shellac referred to in Section V(6) had a particularly bad effect on vulcanization. The following results are for mixes similar to those in Table IV; the shellac mix was still undervulcanized after 100 minutes.

This effect doubtless arises from the high acid value of the bleached shellac (98), and perhaps also from a tendency to split off traces of hydrogen chloride. It would thus appear that shellac bleached by sodium hypochlorite should be used with caution as an ingredient of rubber mixings.

SUMMARY

1. Shellac, even in quite large proportions, can readily be incorporated into raw rubber by the normal process of mixing on a roll mill. It does not assist the breakdown of the rubber during mastication, nor does it show the useful stiffening effect possessed, *e.g.*, by benzidine and *p*-aminophenol. The effects of shellac on plasticity, indeed, are simply what would be expected of a solid that melts to a viscous liquid at about 80° C. The elastic recovery of masticated rubber after deformation is not increased by admixture of moderate proportions of shellac.

Shellac greatly accentuates the calender grain produced by passing unvulcanized rubber between the rolls of a mill or calender. This grain, however, disappears during vulcanization.

2. Shellac does not increase the danger of scorching; indeed, there is evidence that it may exert a useful antiscorching effect, which merits further investigation.

3. Shellac tends to interfere with vulcanization, the attainment of optimum physical properties being retarded and the vulcanizate made weaker and softer. The extent of this interference depends greatly on the composition of the mix, particularly the accelerator. It is probably due largely, though not entirely, to the acidity of the shellac, since it can be reduced by adding a base, *e.g.*, magnesium oxide, or by chemically modifying the shellac to reduce its acidity.

Although the effect is always present, it is not serious in loaded mixes such as are used for most manufactured products, provided a suitable accelerator is chosen. Best results have been obtained with accelerators of the metallic dithiocarbamate class; mercaptobenzothiazole also is good, but diphenylguanidine and especially butyraldehydeaniline generally give poor results.

Shellac can be used in conjunction with alkali-reclaimed rubber just as well as with new rubber.

4. In mixings containing large proportions of fillers or reinforcing agents, *e.g.*, china clay and carbon black, addition of a relatively small proportion of shellac makes the vulcanizate much harder. As the unvulcanized stock is, if anything, softened by this addition, the use of shellac enables very hard vulcanizates to be produced without the processing difficulties that would arise from an attempt to obtain the hardness by using fillers alone. Tests with high carbon black stocks and with china clay flooring or tiling stocks have demonstrated the advantages of this procedure. In the former, abrasion resistance was somewhat impaired by using shellac, but there was evidence of an improvement in flex-cracking resistance, an effect that deserves further investigation.

It is considered that the unexpectedly great hardening effect of shellac in mixes of this type should be more fully studied, in view of its potential utility.

5. Shellac is generally inert towards the aging of vulcanized rubber, and in no case has it been found detrimental.

6. The results obtained in this investigation do not support the claims that have been made to the effect that shellac improves the resistance of vulcanized rubber to swelling by gasoline, benzene, etc., and to absorption of water.

7. Dewaxed shellacs have given better results than TN shellac, as they produce less discoloration in mixes containing zinc oxide, and in some cases give better physical properties. Hard lac resin possesses the same advantages, particularly in the latter respect, but is difficult to disperse, as it does not readily melt. A sample of lac bleached by sodium hypochlorite interfered so seriously with vulcanization that it would probably be unsuitable for use in rubber.

8. Addition of TN shellac, sulfurized lac or hard lac resin to an unloaded (rubber-sulfur) ebonite has not been found to improve the mechanical or electrical properties; indeed, shellac would appear to be unsuitable when a low radio-frequency power loss is required.

9. Mixtures of rubber and shellac containing large proportions of the latter have thermoplastic properties which suggest their use, with or without the addition of fillers, vulcanizing agents, and accelerators of the hardening of shellac, as moulding materials, adhesives, impregnating agents, binders for fibrous materials, etc., and also, in view of the good electrical properties of rubber and shellac, as electrical insulants, particularly to replace gutta-percha. Promising results have been obtained with unvulcanized rubber-shellac mixtures as adhesives for making plywood.

As the present research was concerned primarily with the use of shellac in vulcanized rubber products, these unvulcanized mixtures have not been extensively studied. They are considered to merit a more extended investigation, as they do not appear to have received any attention from scientific investigators hitherto.

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THE COLD-COMPRESSION SETS OF NATURAL AND SYNTHETIC VULCANIZATES *

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The behavior of certain large synthetic rubber gaskets on naval vessels during the past winter points to the necessity for a cold compression-set test in the specifications for these gaskets. It has been found, for example, that Neoprene gaskets on large valves, which perform satisfactorily at temperatures of 60° F and above, are not usable at temperatures of 40° F and below. They take a cold compression-set, while the valves are closed, so that when the valves are opened and then again closed, the leading edge or surface of the valve does not seat properly. This cold compression-set is not permanent; when the gaskets which exhibit cold compression-set are removed to a warm atmosphere (about 80° F), they slowly regain their original shape.

A survey of the literature dealing with the effects of low temperatures on rubber compounds yielded no information on cold compression set. The set test proposed by Morris, James, and Evans[1] in connection with their low temperature stiffness test is not directly applicable to the present problem because it is conducted in tension. Therefore to investigate cold compression-set, it was necessary to devise a new testing procedure.

TESTING PROCEDURE

The new testing procedure is a modification of the A.S.T.M. test for hot compression-set, method B[1]. The standard test-specimen, a cylindrical disk 0.5-inch in thickness and 1.129 inches in diameter, is compressed at room temperature to 40 per cent deflection between two chromium-finished plates. It is held at this deflection by bolting the plates on 0.300-inch thick spacer bars, as shown in Figure 1, and then conditioned for the desired interval in cold methanol. At the conclusion of this interval the specimen is released and allowed to recover for 30 minutes while still in the cold methanol. The specimen is then withdrawn from the cold methanol, and its thickness measured immediately with a dial micrometer. The cold compression-set is expressed as a percentage of the original deflection and is calculated as follows:

$$C = \frac{t_0 - t_1}{t_0 - t_s} \times 100$$

where: C = percentage compression set.

t_0 = original thickness of the specimen, measured at room temperature.

t_1 = thickness of the test-specimen 30 minutes after removal from the clamp, measured at the temperature of the experiment.

t_s = thickness of the spacer bar.

No correction is made for the contraction of the specimen due to cooling; *i.e.*, the original thickness of the specimen is measured at room temperature, not at the temperature of the experiment. Thus, even though the specimen is compressed hot during the conditioning interval, it will apparently take a very slight set. This set was found to be only 1 per cent at 0° F in the case of the *Hevea* vulcanizate, and very much less in the case of the synthetic vulcanizates. Since the error in the compression-set measurement itself is often greater than 1 per cent, the neglect of the correction for contraction due to cooling is justified.
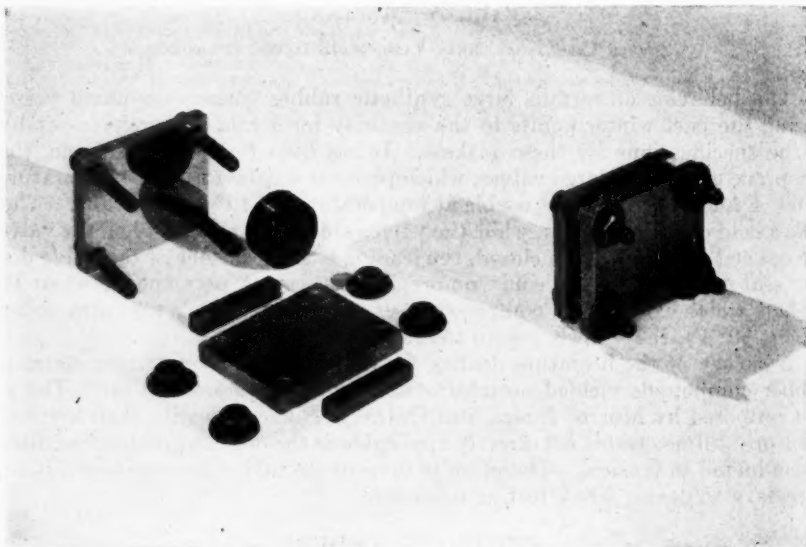
Fig. 1.—Compression set test apparatus—disassembled and assembled.

The cold methanol conditioning tank with its accessory apparatus is shown in Figures 2 and 3. The tank is 4.5 inches in depth and 14 inches in diameter inside. It is provided with an air-powered stirrer. The tank with the coil through which the methanol is pumped to cool is 12 inches in depth and 24 inches in diameter inside. This tank is filled with methanol or mixtures of methanol and water and is cooled with dry ice. The pump, a centrifugal type with $\frac{1}{8}$ h.p. motor, runs continuously. The methanol is either pumped through the cooling coil and then into the conditioning tank, or pumped directly back into the conditioning tank. The direction of pumping is governed by a Tag Celectray indicating controller, which operates the solenoid valves through a a double throw relay. The temperature of the methanol in the tank is thereby maintained constant with a precision of plus or minus 1° C or better. The temperature of the methanol in the conditioning tank is indicated by a toluene-in-glass thermometer and recorded by a Tag Celectray recorder. Both tanks and the connecting pipes are heavily lagged with cork.

STOCKS TESTED

Tests were conducted on four stocks prepared from *Hevea* rubber, GR-S, Perbunan-26, and Neoprene-GN, respectively. The *Hevea* stock was com-

pounded to comply with the requirements of the Navy Department specification for medium soft gaskets from natural rubber[3]. The other stocks were compounded to comply with the requirements of the Bureau of Ships specification for medium soft gaskets from synthetic rubber[4]. The recipes, cures, and some physical properties of the vulcanizates are given in Table 1.

Fig. 2.—Cold methanol conditioning tank and accessory apparatus.

Fig. 3.—Details of cold methanol conditioning tank and accessory apparatus.

TESTS CONDUCTED

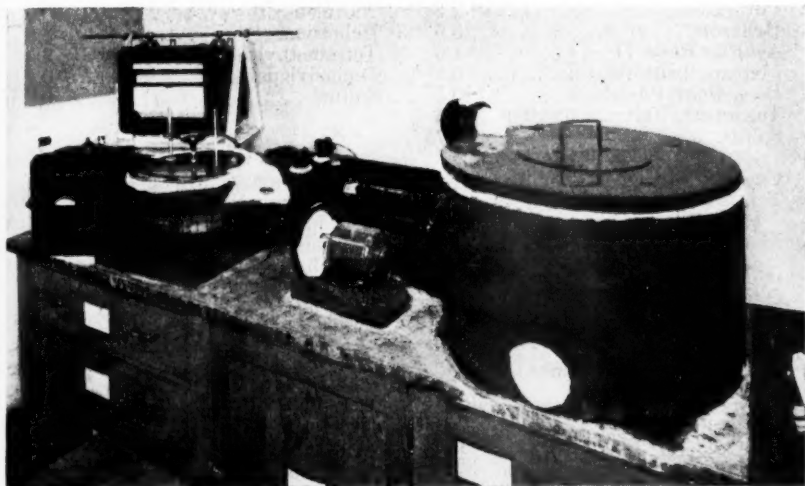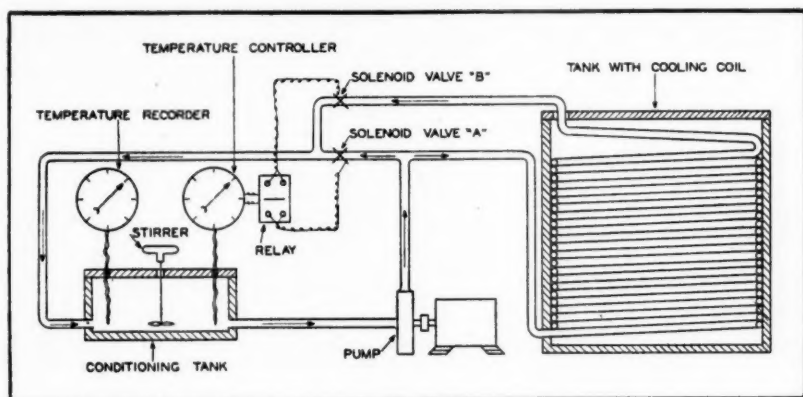Compression sets were determined at 40°, 20°, 0°, and −20° F after conditioning for various intervals up to 70 hours. Compression sets were determined at −40° F after conditioning for various intervals up to 94 hours. All determinations were made in triplicate.

TABLE 1

RECIPES, CURES, AND SOME PHYSICAL PROPERTIES OF VULCANIZATES

Hevea Vulcanizate

Smoked sheet	100.0
Zinc oxide	5.0
Stearic acid	1.0
Cottonseed oil	2.5
Heliozone	3.0
AgeRite Resin D	1.0
Mercaptobenzothiazole	0.5
Benzothiazyl disulfide	0.5
Tetramethylthiuram disulfide	0.5
Sulfur	0.75

Cure: 25 min. @ 287° F
Tensile strength: 3100 lbs. per sq. in.
Modulus at 500% elongation: 450 lbs. per sq. in.
Ultimate elongation: 770%
Shore hardness ($\frac{1}{4}$-inch thickness): 32

GR-S Vulcanizate

GR-S (Torrance)	100.0
Zinc oxide	5.0
Statex-B	50.0
Naftolen-510	20.0
Heliozone	3.0
Tetramethylthiuram sulfide	2.0
Diphenylguanidine	0.4
Sulfur	0.6

Cure: 25 min. @ 310° F
Tensile strength: 1860 lbs. per sq. in.
Modulus at 500% elongation: 870 lbs. per sq. in.
Ultimate elongation: 790%
Shore hardness ($\frac{1}{4}$-inch thickness): 44

Perbunan Vulcanizate

Perbunan-26	100.0
Zinc oxide	5.0
Statex-B	30.0
P-33 black	30.0
Stearic acid	1.0
Heliozone	3.0
Tributoxyethyl phosphate	10.0
Plasticizer-SC	10.0
Tetramethylthiuram disulfide	3.0
Mercaptobenzothiazole	2.0
Selenium	0.1

Cure: 30 min. @ 310° F
Tensile strength: 2020 lbs. per sq. in.
Modulus at 500% elongation: 690 lbs. per sq. in.
Ultimate elongation: 910%
Shore hardness ($\frac{1}{4}$-inch thickness): 45

Neoprene Vulcanizate

Neoprene-GN	100.0
Zinc oxide	10.0
Litharge	20.0
Thermax	20.0
Stearic acid	1.0
Paraffin	2.0
A-1 White substitute	10.0
Circo Light Process Oil	10.0
Neozone-A	2.0

Cure: 85 min. @ 310° F
Tensile strength: 1830 lbs. per sq. in.
Modulus at 500% elongation: 720 lbs. per sq. in.
Ultimate elongation: 780%
Shore hardness ($\frac{1}{4}$-inch thickness): 47

To find the effects of higher temperatures, compression sets were determined also at 60°, 80°, 120°, 160°, and 200° F after 70 hours at each temperature. These determinations were likewise made in triplicate. The conditioning was done in the methanol bath at 60°, at a constant temperature room at 80°, and in an oven with forced circulation at 120°, 160°, and 200° F. In every case the procedure for handling the test-specimens was the same as described previously. The specimens were allowed to recover for 30 minutes at the temperature of the experiment after release from the clamps.

EFFECT OF METHANOL

The volumes of the specimens were determined at room temperature with a Jolly balance before and after the 70-hour compression-set test at 40° F. These determinations were advisable because significant swelling or shrinkage

of the specimens would complicate the interpretation of the compression set data.   The results of these determinations, given in Table 2, indicate that the

TABLE 2

VOLUME CHANGE OF COMPRESSION SET SPECIMENS IN METHANOL
AT 40° F WHILE UNDER 40% DEFLECTION

Vulcanizate	Volume Change (percentage)
Hevea	+0.2
GR-S	+0.3
Perbunan	+2.0
Neoprene	0.0

methanol had a negligible effect at 40° F on the volumes of the specimens. It would be expected to have even less effect at lower temperatures.

The compression-set tests at 40° F were repeated in an Aminco Sub-Zero test cabinet, Figure 4, which was cooled with dry ice.   The specimens were
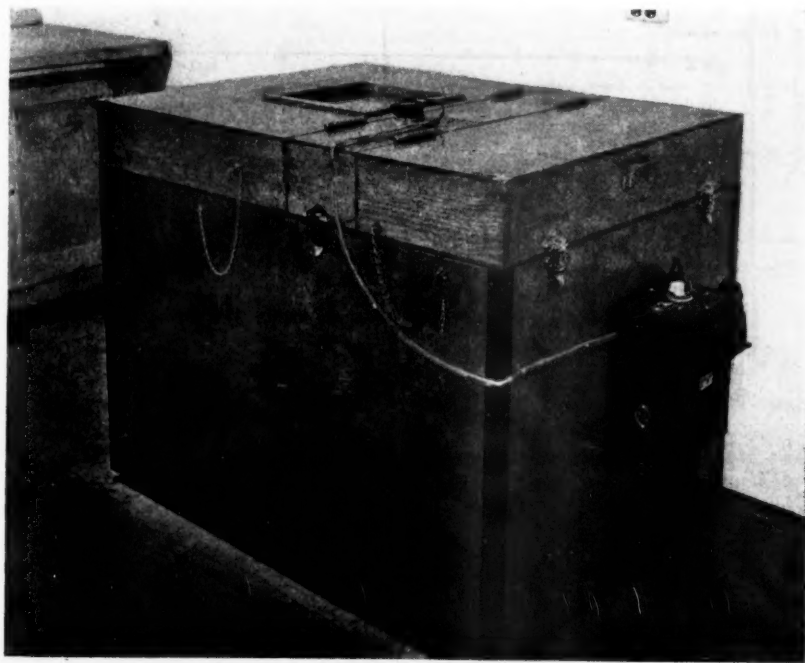
FIG. 4.—Aminco sub-zero test cabinet.

conditioned in an atmosphere of carbon dioxide gas instead of in cold methanol, as formerly.   These tests were conducted as a further check on the effect of methanol and also to determine the practicability of using the Aminco cabinet. Inasmuch as the cabinet had to be left open while the specimens were being released from the clamps, and then again 30 minutes later while the specimens were being removed for measuring, the specimens had more opportunity to warm up than they did when conditioned in cold methanol.   However the

comparative data, plotted in Figure 5, show good agreement between tests performed in carbon dioxide and methanol. These results prove that the methanol had a negligible effect on the specimens and that a cold box such as the Aminco cabinet can be used for the compression set tests. If the cold box were provided with arm holes and sleeve gauntlets, and with a micrometer gage
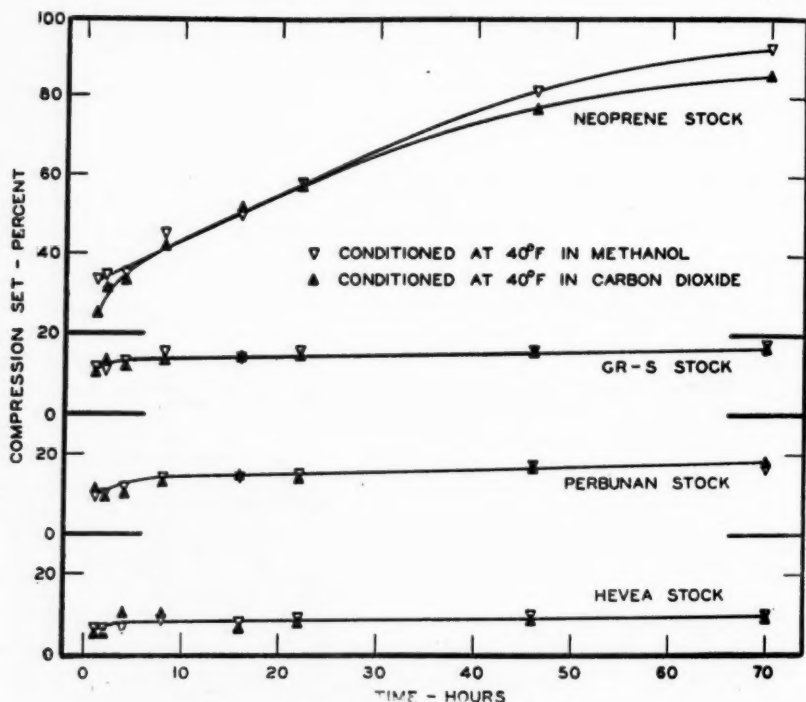
Fig. 5.—Comparison of conditioning media.

to measure thickness, perfect conditions would be obtained for this test since the specimens would not be exposed to higher temperatures at any time during the test.

RESULTS OF TESTS

The cold compression-set data obtained in cold methanol are plotted *versus* conditioning intervals in Figures 6, 7, 8, 9, and 10. These graphs show that the GR-S and Perbunan vulcanizates soon attained, at each temperature, values for compression set which remained virtually constant as the conditioning intervals were lengthened. These values, which were practically the same for both vulcanizates, increased as the temperature was lowered.

The *Hevea* vulcanizate behaved in the same manner as the GR-S and Perbunan vulcanizates at 40° and 20° F, although its compression-set values at these temperatures were lower than the corresponding values for the other vulcanizates. At 0°, −20°, and −40° F, the behavior of the *Hevea* vulcanizate changed radically; its compression set, while initially much lower than the compression sets of the other vulcanizates, increased in the form of an S-shaped
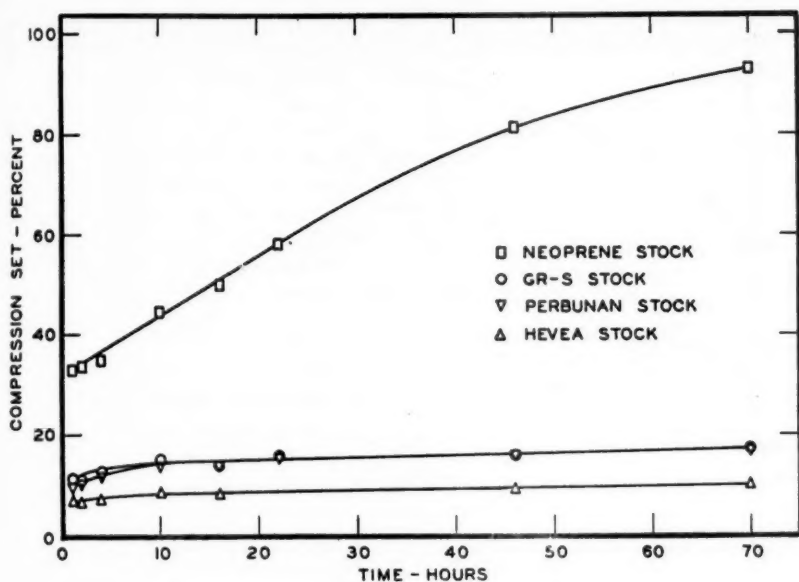
Fɪɢ. 6.—Compression sets at 40° F vs. conditioning intervals.
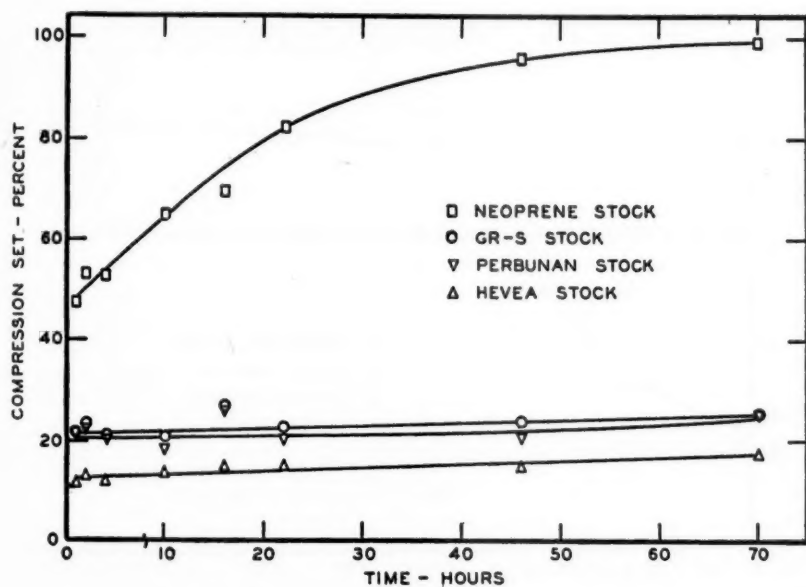
Fɪɢ. 7.—Compression sets at 20° F vs. conditioning intervals.
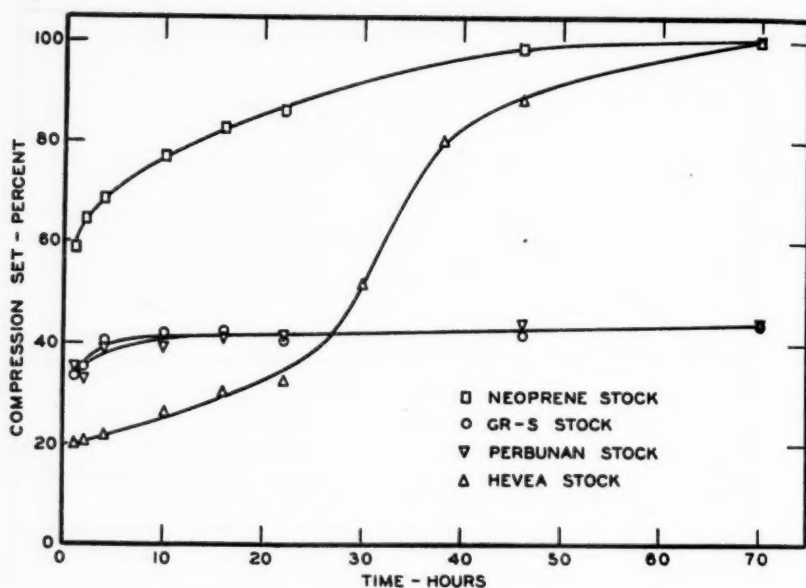
FIG. 8.—Compression sets at 0° F vs. conditioning intervals.
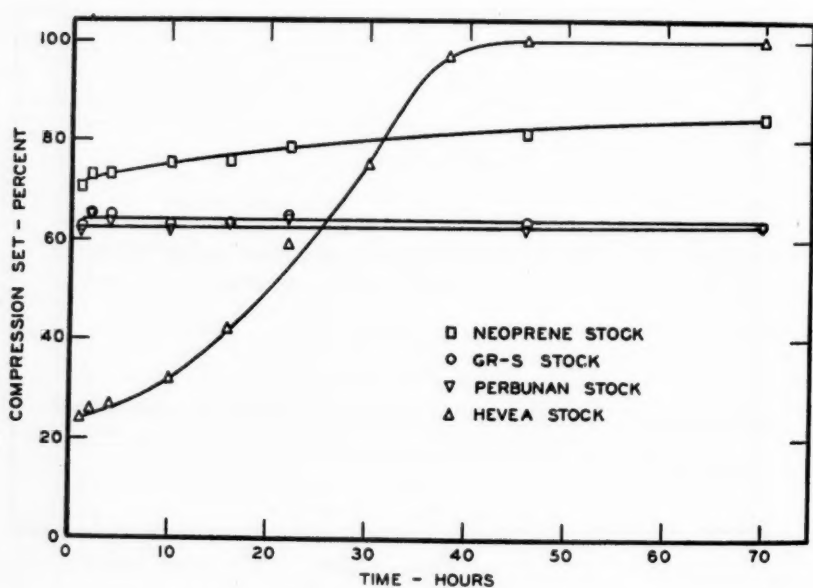
FIG. 9.—Compression sets at −20° F vs. conditioning intervals.

curve and approached 100 per cent as the conditioning interval was lengthened. Its compression set reached 100 per cent in 70 hours at 0° F and in 46 hours at −20° F, but it did not quite reach this value in 94 hours at −40° F.

The Neoprene vulcanizate had initially the highest compression set at all temperatures except −40° F.   At 40°, 20°, and 0° F, its compression set increased and approached 100 per cent as the conditioning interval lengthened. The rate of increase was somewhat greater as the temperature was lowered. At −20° F, the compression set of the Neoprene vulcanizate increased very gradually as the conditioning interval lengthened.   This curve can be seen in Figure 9 to have the same shape as the GR-S and Perbunan curves except that its slope is somewhat greater.   At −40° F, the compression sets of the GR-S, Perbunan, and Neoprene vulcanizates were almost identical at all time intervals.
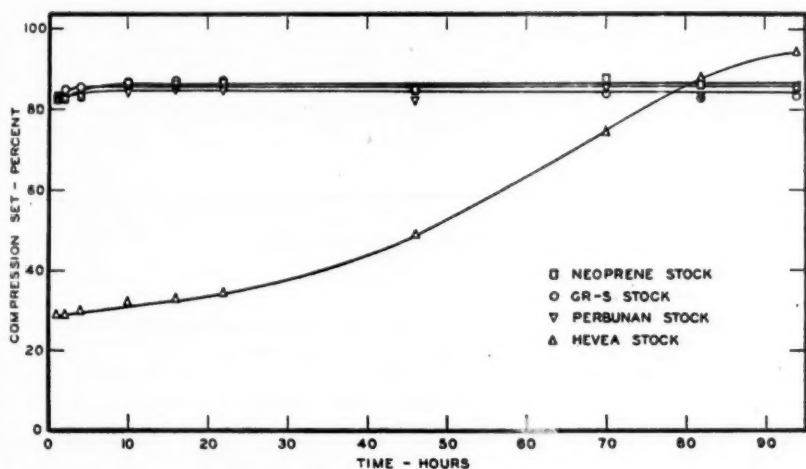
Fig. 10.—Compression sets at −40° F vs. conditioning intervals.

The compression sets of the four vulcanizates are plotted *versus* temperature in Figure 11 over the range −40° to 200° F.   The compression sets were measured after 70 hours' compression and 30 minutes' recovery in the conditioning medium.   The compression sets of all the vulcanizates reached minimum values at room temperature.   The compression set of the Neoprene vulcanizate was higher above and below room temperature than the compression sets of the other vulcanizates.   Both the GR-S vulcanizate and the Perbunan vulcanizate had less compression set than the *Hevea* vulcanizate at 0° and −20° F.   The GR-S vulcanizate also had less compression set than the *Hevea* vulcanizate above 120° F.

RECOVERY OF SPECIMENS

It is noteworthy that, in contrast to hot compression-set, cold compression-set was found to be a reversible phenomenon.   When the specimens which exhibited cold compression set were warmed to room temperature, they recovered their original shape.   The compression sets were even of transitory nature at low temperatures in the case of the GR-S and Perbunan vulcanizates.
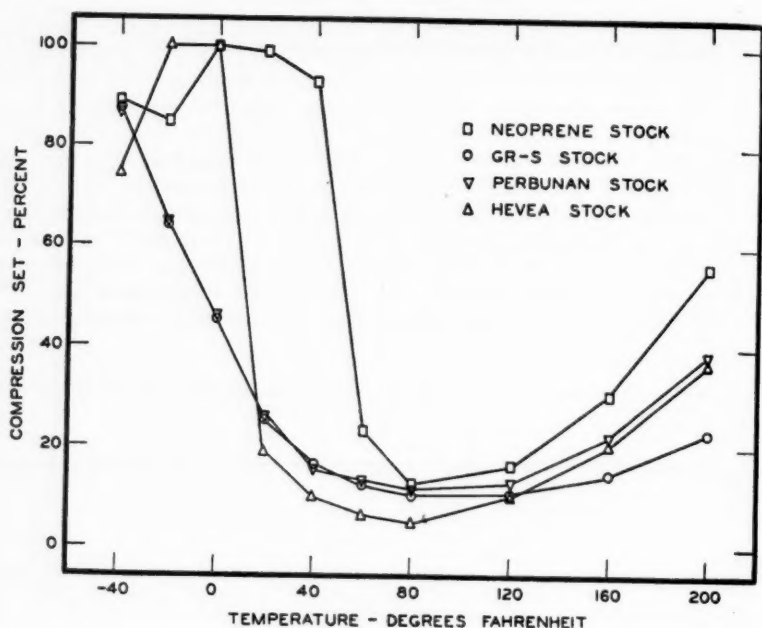
Fig. 11.—Compression sets after 70 hours' conditioning at various temperatures.

A graph showing the recovery in methanol at 0° F of specimens which had been subjected to 70 hours' compression at this temperature is given in Figure 12. It will be noted that the GR-S and Perbunan specimens had recovered considerably after 96 hours, although the *Hevea* and the Neoprene specimens remained
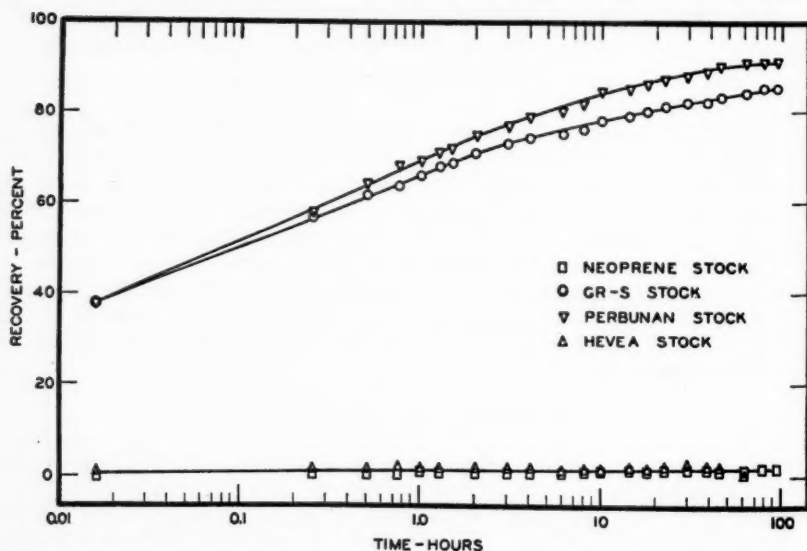
Fig. 12.—Recovery in methanol at 0° F after 70 hours' compression at 0° F.

unchanged. Therefore, when presenting cold compression-set figures, it is advisable to specify the relaxation time between release and measurement of the specimens

INTERPRETATION OF RESULTS

The behavior of the specimens in the cold compression-set tests can be explained on the bases of internal viscosity, tendency to crystallize, and rate of crystallization. All rubberlike bodies have internal viscosity, *i.e.*, they do not assume immediately their final deformation when subjected to a force, and they do not recover immediately their original shape when the force is removed. In this respect they have been compared with a steel spring whose movements are damped by a viscous liquid[5]. The slowness with which rubberlike bodies recover after deformation is accentuated by decreasing the temperature because internal viscosity is an inverse function of temperature. Thus, cold compression-set as here measured can be regarded as a criterion of internal viscosity, at least for the GR-S and Perbunan vulcanizates tested, since the amount of set found is a function of the time between release and measurement of the specimen (Figure 12)

The change of internal viscosity with temperature does not explain the behavior of the *Hevea* and the Neoprene vulcanizates at low temperatures. These vulcanizates had two characteristics which differentiated them from the GR-S and Perbunan vulcanizates: they tended toward 100 per cent cold compression-set at some temperatures, and they did not gradually recover their shape when released and kept at the low testing temperature (Figure 12). These characteristics can be explained by assuming that the *Hevea* and the Neoprene specimens actually crystallized under the conditions of the test.

Katz[6] found that stretched *Hevea* rubber exhibits a crystalline fiber diagram when examined with x-rays. Carothers and his co-workers[7] found the same for Neoprene. Sebrell and Dinsmore[8] found no evidence for a crystalline fiber diagram when Buna-S and Buna-N were stretched. The latter rubbers are similar to GR-S and Perbunan, respectively.

These observations explain what happened to the Neoprene and the *Hevea* vulcanizates in the present investigation. When the specimens were compressed, they were effectively stretched in a plane normal to the direction of pressure. The Neoprene specimens tended to crystallize in the plane of stretching at 40°, 20°, 0°, and −20° F. The *Hevea* specimens tended to crystallize in the plane of stretching at 0°, −20°, and −40° F. The rate of crystallization reached a maximum at 0° F for the Neoprene specimens and at −20° F for the *Hevea* specimens. The crystalline formation prevented these specimens from recovering as long as the temperture was not raised.

It is recognized that the *Hevea* vulcanizate and the Neoprene vulcanizate can crystallize without being deformed. Bekkedahl and Wood[9] demonstrated by measurements in a dilatometer that *Hevea* stocks vulcanized with small amounts of sulfur or with tetramethylthiuram disulfide crystallize at 35° F, even though not distorted. Forman[10] studied the hardness changes of *Hevea* and Neoprene vulcanizates at low temperatures and ascribed some of the changes to crystallization.

The present authors followed the hardness changes at low temperatures of the *Hevea* and the Neoprene vulcanizates described herein by means of a Rex gauge. The Rex gauge gave instantaneous hardness readings with only momentary contact; therefore the specimens were not appreciably warmed during

the measurements.   Uncompressed specimens ½-inch thick of both vulcanizates were immersed into the cold alcohol bath at various temperatures and for various times up to 94 hours.   Their hardness was determined immediately after removal from the bath.

It was found that both vulcanizates exhibited the rate of increase in hardness which would be expected if crystallization occurred, *i.e.*, the hardness gradually increased with time and finally leveled off at a high value, indicating maximum crystallization.   The time to reach maximum crystallization, however, was longer than when the specimens were deformed.   For example, the hardness of the *Hevea* specimens attained and leveled off at 90 after 70 hours at $-20°$ F; whereas the compression set of the *Hevea* specimens reached a value of 100 per cent in 46 hours at this temperature.

In conclusion it should be emphasized that two kinds of cold compression-set have been found.   One kind is a reversible phenomenon under isothermal conditions; the amount of retained deformation depends on the time interval between release and measurement of the specimen.   The other kind is largely a nonreversible phenomenon under isothermal conditions; a proportion of the deformation is retained indefinitely after release of the specimens.

ACKNOWLEDGMENT

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FREE AND FORCED VIBRATION METHODS IN THE MEASUREMENT OF THE DYNAMIC PROPERTIES OF RUBBERS*

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INTRODUCTION

In a previous paper[1] a method has been described for the measurement of the dynamic elastic compression modulus of elasticity and the associated resilience of rubberlike materials. In this method vibrations were excited by means of a rotating unbalanced mass in a mass-spring system which consisted of a light angle-iron cage supported by four rubber compression springs. The speed of the rotating mass was varied until a resonant vertical vibration was observed, and by a well known method[2] values were then calculated for the dynamic compression modulus and the resilience of the rubber contained in the supporting mountings.

The quantity 'resilience' is usually defined for rubber as the ratio of a wave amplitude to that immediately preceding it in a train of damped free vibrations. The logarithmic decrement, which is the quantity more generally used to characterize the decay of free vibrations, is then the natural logarithm of the inverse of the resilience, as defined above. With this definition, the most direct measurement of resilience would then appear to be based on free vibration experiments[3]. However, it is possible to express the resilience in terms of the results obtained in forced vibration resonance experiments, on the assumption that the mechanical loss in rubber may be described by a 'normal viscosity' factor[4]. The comparison between the two methods is based on the use of a simple mechanical model for rubber, consisting of a purely elastic spring with a dashpot in parallel. Experimental justification for this hypothesis has been published by a number of workers[5]. Most of the experiments have shown that the viscosity varies inversely with frequency and this is, therefore, taken as axiomatic in the calculation of theoretical resonance curves made below. The present experiments were undertaken to obtain, on the same test-pieces and the same mechanical system, measurements of resilience by both free vibrations and resonant forced vibrations and, hence, to give experimental justification for the use of the latter method for the measurement of this quantity.

APPARATUS AND METHOD

An electrical vibrator of the type described by a number of previous workers[6] was used in these experiments and is illustrated diagrammatically in Figure 1. It consists essentially of a steel bar A carrying at each end a coil B wound on a

thin Tufnol former, each coil being disposed in the annular gap of a large loud-speaker magnet C, the bar being supported and maintained centrally by flat steel springs D. The test-pieces consist of a pair of flat rubber cylinders firmly bonded to steel plates by the brass plate method[7], the inner plates being rigidly clamped to the center of the bar, the outer to the massive base. Forces tending to vibrate the rubber in shear are exerted when an alternating current is passed through either of the coils and, conversely, an alternating e.m.f. is set up in either coil when the system is caused to vibrate by any external means.
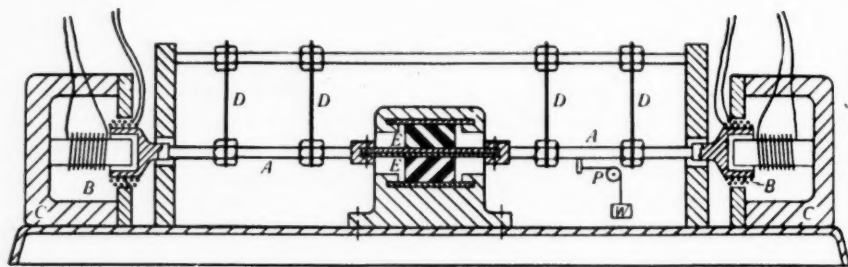
FIG. 1.—Diagram of apparatus for measurement of dynamic properties of rubbers

For the forced vibration experiments, the output from a variable frequency oscillator is amplified and fed to one coil (where large forces are required, the alternating current may be fed to the two coils wired in series); by varying the frequency, the mechanical resonance of the system may be found by observing with a microscope the vibration of a point on the bar. The resonant frequency, the driving current, the mass of the suspended system, and the resonant amplitude are noted. A calibration is carried out of force produced by a unit current, by passing a direct current through one or both coils and balancing the resultant force by weights W supported on a cord passing over a pulley P, as indicated in the diagram, the other end of the cord being attached to the horizontal bar. This calibrating device is, of course, removed once calibration has been effected. All information for the calculation of dynamic shear modulus and resilience is then known.

If a harmonic force $F \sin pt$ is applied to the system, its motion, assuming for the rubber the model described above, is governed by the equation:

$$M \frac{d^2x}{dt^2} + K \frac{dx}{dt} + Sx = F \sin pt \qquad (1)$$

where M is the mass, x the instantaneous displacement of the system, K the damping coefficient, and S the stiffness of the composite system of rubber and steel supporting springs. The complete solution for Equation (1) is the sum of the free and forced vibration solutions. As is well known, the latter corresponds to the steady-state movement under the applied harmonic force after transient effects have died off. The former is obtained by equating the left-hand side to zero.

In the steady-state motion the system executes forced vibrations of am-plitude:

$$A = F / \{(S - Mp^2)^2 + K^2 p^2\}^{\frac{1}{2}} \qquad (2)$$

When the frequency of the applied force is varied, the amplitude of these

vibrations passes through a maximum A_r which is reached at the resonant frequency ν_r where:

$$\nu_r = \frac{p_r}{2\pi} = \frac{1}{2\pi}\left(\frac{2S - K^2}{2M}\right)^{\frac{1}{2}}$$

in the case of the rubbers at normal temperature $K^2 \ll 2S$.

Hence

$$\nu_r = \frac{1}{2\pi}\left(\frac{S}{M}\right)^{\frac{1}{2}} \tag{3}$$

and

$$A_r = \frac{F}{Kp_r} = \frac{F}{2\pi K\nu_r} \tag{4}$$

From Equations (3) and (4), we can find S and K. The dynamic shear modulus of the rubber s is connected with the stiffness of the system S by the following relation:

$$s = (S - S_1)2d/\pi D^2 \tag{5}$$

where S_1 is the stiffness of the supporting steel springs and d and D are the thickness and diameter of the rubber test-pieces. In the same way the coefficient of normal viscosity of the rubber is given by:

$$\eta = K2d/\pi D^2 \tag{6}$$

The equation governing the free vibrations of the system, obtained by equating the left-hand side of (1) to zero, leads to a decay factor $\exp(-Kt/2M)$. The resilience R is equal to the percentage decay in amplitude during the time of one free vibration (which is very nearly equal in frequency to the resonant frequency in the forced vibration experiment). Hence the resilience can be expressed in terms of the quantities measured in the forced vibration experiment, using equations (3) and (4), *i.e.*:

$$R = 100e^{-K/2M\nu_r} = 100e^{-\pi F/SA_r} \tag{7}$$

Alternatively, the expression for the logarithmic decrement is:

$$\delta = \pi F/SA_r \tag{8}$$

To make measurements of resilience directly from the decay of free vibrations, the apparatus described above was used in the following way. An electronic pulse generator which has been designed to control the flashing of a stroboscopic lamp was employed to produce repeated discharges of a neon lamp, the discharge current being passed through one of the loud-speaker coils of the apparatus. The frequency of the pulse could be adjusted so that it was a convenient submultiple of the natural frequency of the mechanical system. After the extinction of a discharge, the neon lamp possessed a very high resistance, so the coil was effectively open circuited. Thus, following the mechanical pulse, the system was able to vibrate freely, damped only by the viscous element of the rubber. The second loud-speaker unit was used as an electromagnetic pick-up and connected though an amplifier of high input impedance to the Y-plates of a cathode-ray oscillograph, whose time base was synchronized to the pulse frequency. As is well known, the output of such a pick-up is proportional to velocity and, hence, to the frequency at constant amplitude. It was found that when it was amplified directly, this increase of response with fre-

quency introduced a source of error due to the relative magnification of the high frequency free vibrations of the metal parts of the equipment excited by the sharp pulse. Consequently, an integrating circuit (shown in Figure 2) was

50,000 ω

Pick-up coil

0·025 μF.

Amp.

C.R.O.

Time base locked to driving pulse
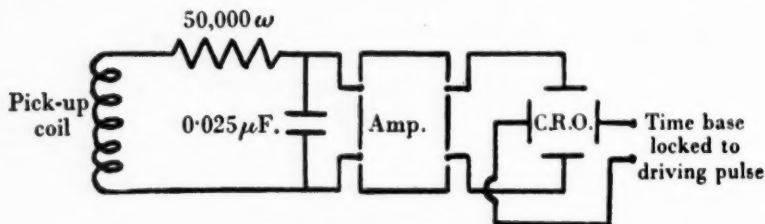
FIG. 2.—Pick-up circuit showing integrating circuit between pick-up and amplifier

connected between the pick-up and the oscillograph amplifier, so that the input to the latter was proportional to the amplitude of the vibration and independent of frequency.

In this manner, periodic trains of damped oscillations were impressed on the screen of the oscillograph. The period of these trains, to which the time base of the oscillograph was synchronized, was that of the pulse generator. Consequently, the persistent image of a damped series of oscillations was obtained. The frequency of these damped oscillations was equal to the natural frequency of the mechanical system, the number of oscillations then being equal to the ratio of this frequency to the frequency of the pulse generator. By covering the end of the oscillograph tube with a transparent screen carrying square mesh rulings, the amplitudes of successive waves could be observed and the resilience calculated for each pair of adjacent waves. In practice more accurate results were obtained by photographing the trace and measuring the amplitude on the negative with a travelling microscope.

RESULTS

To compare results obtained by the two methods, measurements were carried out of three compounds designated A, B and C. A was a natural rubber compound with a fairly low loading of carbon black and a nominal hardness of 50° (Shore). B was a GR-S compound, nominally 60° hardness (Shore), and C was a GR-S-natural rubber (50/50) compound of nominal hardness 50° (Shore). All three were commercial compounds used in antivibration mountings.

Figure 3 shows the forced vibration results on A, the experimental points being plotted. The experimental curve through these points (not shown) led to values for dynamic shear-modulus and viscosity coefficient. From these two figures, assuming that the viscosity coefficient varies inversely with frequency as has been demonstrated by previous workers[5], the theoretical resonance curve was calculated from Equation (2) and is given in Figure 3. The proximity of the experimental points to the theoretical curve indicates that the assumed model for the mechanical behavior of this type of rubber is well justified. The resilience for rubber A was then calculated by Equation (7).

The resilience was obtained also from the free vibration experiment. To estimate the accuracy of this method of measurement, it was obtained for the successive amplitudes of the damped oscillations. The results are given in
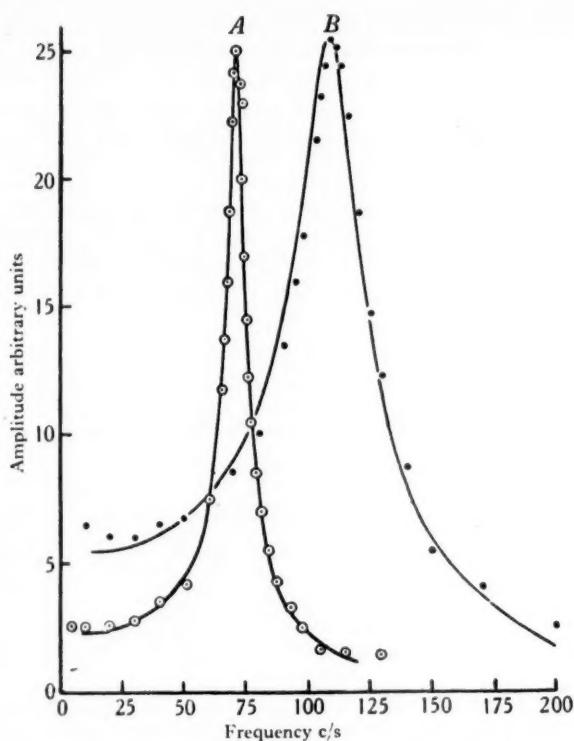
Fig. 3.—Experimental points and theoretical resonance curves for rubbers A and B
Frequency c/s

Table 1, together with the average value for the resilience, while a photograph of the oscillograph trace is shown in Figure 4.

A   B   C
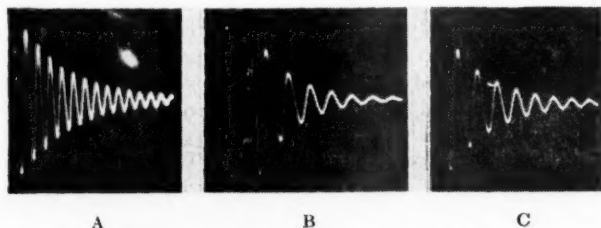
Fig. 4.—Free vibration oscillograms for rubbers A, B and C

In a similar way the experimental points and theoretical resonance curve for B are shown in Figure 3.   It will be seen that the experimental results for B in Figure 3 show the typical asymmetrical peak characteristics of a nonlinear spring[8].   This effect has been demonstrated for some types of rubber under similar conditions by previous workers[9].   The free vibration results on material B are given in Table 1, and a typical trace is shown in Figure 4.   The more rapid rate of decay of the vibration for specimen B compared with A is obvious from a comparison of their respective traces.

Rubber	Resilience values (per cent)	Mean %
A	76.4, 77.8, 77.6, 76.8, 77, 76.4, 77.8, 78.7, 76.6, 77.4, 73.7	76.9
B	55, 55.6, 53.6, 55.1, 58.1, 55, 53.5, 56.7, 50.9, 54.1	54.3
C	65.3, 67, 66.1, 64.1, 65.1, 66.1, 66.0, 64.7	65.6

The results of the forced vibration experiment on material C gave values of dynamic shear modulus and resilience equal to 12.0 dynes $\times 10^6$ per sq. cm. and 64 per cent, respectively, and the experimental points again agreed very well with the calculated resonance curve. Table 1 shows the free vibration results and Figure 4 a typical trace.

DISCUSSION

The comparison of the resilience results obtained by the two methods is given in Table 2. The resilience, calculated by means of Equation (7) from

TABLE 2

COMPARISON OF RESILIENCE VALUES FROM FREE AND FORCED VIBRATIONS

Rubber	Shear modulus (dynes per sq. cm.)	Resilience from free vibration (percentage)	Resilience from forced vibration (percentage)
A	9.0×10^6	76.9	75.5
B	21.6×10^6	54.3	50.1
C	12.0×10^6	65.6	64

the values of the dynamic shear modulus and viscosity coefficient obtained by the forced vibration experiment, is compared with the average resilience value obtained by free vibration experiments for each of the three rubber qualities, A, B and C. It is seen that values of resilience thus obtained agree within the limits of experimental error in the above measurements, and thus justify the application of the simple mechanical model described above, with the additional assumption that the viscosity coefficient is not constant, but inversely proportional to frequency. The justification of such a model on the basis of the molecular structure of highly elastic polymers, requires further investigation; it is obvious, however, that it gives a useful macroscopic description of the elastic properties of high polymers, and forms a sound working basis for their application to vibration and other mechanical problems.

ACKNOWLEDGMENTS

SUMMARY

Previous work on the shear elastic modulus and damping factor of rubber has been carried out chiefly by two methods. Some workers have deduced these quantities from the natural frequency and rate of decay of the free vibrations of a simple system comprising a mass and a rubber spring; others have

obtained the values from the resonance curve of such a system under forced vibration excited by a known harmonic force of variable frequency.   The derivation of the shear modulus and damping factor from the experimental results is in both cases based on the assumption for rubber of a simple mechanical model consisting of a spring with a viscous dashpot in parallel.   In order to ascertain whether the results from the two methods (more particularly for the damping factor) correspond, measurements have been carried out by both methods on the same rubber test piece on the same mechanical system and under identical conditions.   The approximate agreement between the results thus obtained justifies the basic assumptions underlying these methods.

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A MODIFIED METHOD FOR THE DIRECT ESTIMATION OF THE ABSORPTION OF OXYGEN BY RUBBER*

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INTRODUCTION

The importance of the direct estimation of the absorption of oxygen by rubber became evident from the research work of Dufraisse and his collaborators. Dufraisse[1] designed a very useful apparatus for this purpose; it is based on the manometric method, by which comparative relative determinations can be applied fairly quickly to about ten samples of rubber.

Although a relative estimation of this kind suffices for many technical and scientific purposes, some scientific problems may require a knowledge of the exact quantity of oxygen absorbed. The following formula, evolved by Chovin[2], for the calculation of the absolute measure of this oxygen absorption from the mercury rise curve will be found convenient:

$$v = h \left[s + \frac{V - sh}{76} \right]$$

where v = volume at 1 atmosphere of the oxygen absorbed at the temperature of the test.

h = mercury rise.

s = diameter of the manometer tube.

V = original volume of gas in the absorption vessel.

This computation, however, is rather complicated and is not very exact, for the reason that oxidation in the Dufraisse apparatus takes place neither at constant volume nor at constant pressure. For, when the absorption begins and the mercury is down at the base of the manometer tube, the volume is greater by approximately 15 to 20 per cent than at the end of the determination, so that the rise at the end should be 15 to 20 per cent quicker. Then again, the oxygen pressure after 30 cm. mercury rise is about 0.6 atmospheres. It is now known, however, from investigations by Milligan and Shaw[3], and confirmed by the present author, that the absorption of oxygen is approximately proportional to the square root from the oxygen pressure. Calculation from this shows that the absorption of oxygen at 0.6 atmospheres is roughly 80 per cent of the absorption at 1 atmosphere. The result of the two effects added together is that the *rise of the mercury* in the manometric method is practically independent of the pressure, from which fact Morgan and Naunton[4] concluded wrongly that the absorption of oxygen is independent of the pressure.

Where, therefore, relative measurements do not suffice for the purpose in hand, some other method must obviously be sought for. The most likely resort would be, then, to make the determinations at constant pressure, as did

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170

formerly Kohman[5] and Milligan and Shaw[3].   However, Kohman's instrument is fairly complicated, while measurements with Milligan and Shaw's apparatus can be taken only with air.   So far as ease of handling and rapidity of determination are concerned, both devices are far inferior to that of Dufraisse.

The method now to be described is based on a combination of the principle of constant pressure determinations and the convenient facilities provided by Dufraisse's instrument.

DESCRIPTION OF THE APPARATUS

The entire apparatus, consisting of 12 measuring units, is illustrated in Figure 1, while Figure 2 depicts one measuring unit in detail.
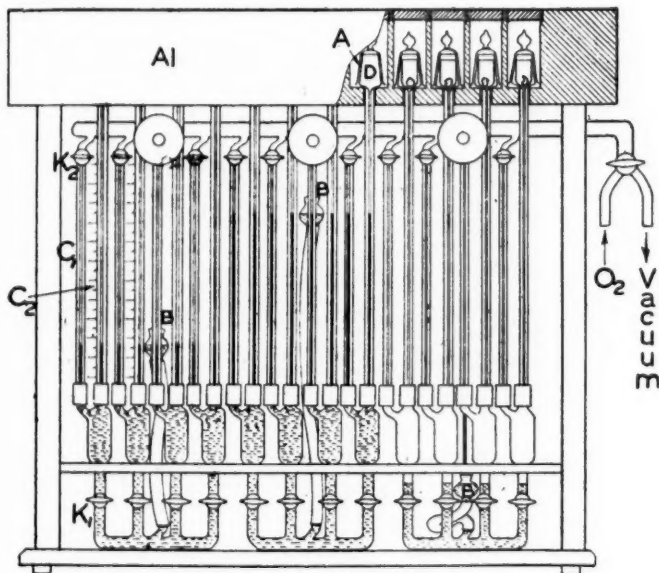
Fig. 1.—The entire oxygen absorption apparatus with 12 units.

A unit consists of an absorption vessel A, containing a glass cap D with rubber, connected to a gas meter.   As in Dufraisse's apparatus, these absorption vessels are placed in an electrically heated aluminum block Al, which can be maintained at exactly 80° C, or at any other temperature desired by means of a mercury regulator connected to a relay.   The gas meter consists of a capillary tube C (inside diameter 2 mm.) connected to a second similar tube placed next to it, and to a movable mercury reservoir B.

At the beginning of the test, B is set low, cock K_1 is closed, and the entire apparatus is evacuated after C_2 and C.   This at the same time facilitates the detection of leakages, if any.   Along the same channels the whole tube is filled with oxygen at a pressure (a few cm. Hg pressure less than 1 atmosphere) to ensure that, after opening cock K_1, raising reservoir B and connecting tube C_2 with the outside air, the mercury stands a little way in tube C_1.   So far the procedure would seem to differ little from that of the Dufraisse apparatus, but the essential difference is that, in the apparatus now described, a

pressure of 1 atmosphere is made to prevail in the absorption vessel during the process of absorption. To this end reservoir B is constantly being raised so that the mercury level in tubes C_1 and C_2 remains the same.

In practice this adjustment of the mercury level can be made to coincide with a reading, say, every hour. Meanwhile the pressure is, admittedly, a little below 1 atmosphere, but if care is taken not to allow the difference in pressure in the tubes to exceed 1 cm. pressure, the resulting slight error remains well within the error of measurement. The advantage of this expedient is that
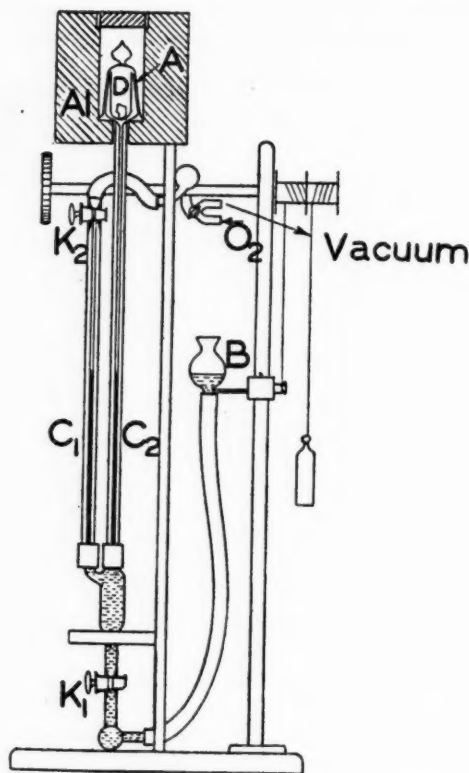
Fig. 2.—Unit of the oxygen absorption apparatus.

a direct reading of the absolute absorption of O_2 can be taken at the end of the test, provided capillary C has been previously calibrated. For example, let 1 cm. capillary have a volume of 0.03 cu. cm., and the mercury rise 5 cm. in one hour; then the rubber has absorbed, $5 \times 0.03V = 0.15$ cm³/O_2, which now need only be reduced from room temperature to 0° C. There are three reservoirs B connected to the whole apparatus, each of which, therefore, serves four absorption vessels. To ensure accurate adjustment, each reservoir is suspended from a pulley, which can be made to revolve by hand, thus raising or lowering the reservoir. The mercury in every tube can then be adjusted individually with the aid of cocks K.

The pipelines for gas and vacuum of all twelve vessels are interconnected so that all the tubes can be rinsed out and filled with oxygen at the same time, which takes only a few minutes. Moreover, by using cock K_2, each unit can itself be connected or disconnected. A second advantage is that the rise of mercury in one and the same tube is approximately four times quicker by the constant pressure method than by the manometric method, though otherwise under the same conditions, owing to the fact that the absorbed gas is taken from the gas in the capillary only. For, according to Chovin's formula[2], 1 cm. mercury rise in a manometer tube of the Dufraisse apparatus corresponds roughly to the absorption of 0.013 cc. of oxygen, whereas, by the method here described, the mercury has then risen more than 4 cm., since the volume of gas of 1 cm. capillary amounts to 0.03 cc. If one wishes to follow the manometric method, all that is necessary is to leave reservoir B down below so that the mercury rises only in tube C_1, and not in tube C_2.

The shape of the absorption vessel[6] is very different from that used by Dufraisse, though it has no further bearing on the method of procedure. This vessel, with a volume of 8 cc., consists entirely of glass, and is directly connected, through an opening at the base of the aluminum block, with the capillary tube. It is sealed by means of a ground-in piece which surrounds the whole vessel, while the ground-in piece is sealed off with a thin layer of asphaltic bitumen. The advantage of this absorption vessel is that it can easily be kept clean.

SOME RESULTS

The results of all measurements are recorded in cc. of oxygen of 0° C and 76 cm. mercury pressure per gram of rubber per hour, measured at T° and 1 atmosphere pressure.

Several determinations were applied to a rubber mixture No. 1 to establish reproducibility.

The mixture was composed as follows: crepe 100 parts, S 3.5 parts, diphenylguanidine 0.5 parts, and ZnO 5 parts, vulcanized for 20 minutes at 147° C.

Fivefold measurements were carried out, each with 1 gram of rubber divided into blocks of $2 \times 2 \times 2$ mm. Very good check values were obtained, as the values in Table 1 show. The influence of the oxygen pressure can also

TABLE 1

RESULTS OF MEASUREMENTS IN THE OXYGEN ABSORPTION APPARATUS WITH MIXTURE No. 1

Temp.	Gas	Absorption in cc.						
80° C	oxygen	0.14	0.14	0.14	0.15	0.14	Average 0.14	cc.
90° C	oxygen	0.27	0.28	0.28	0.28	0.28	Average 0.28	cc.
100° C	oxygen	0.66	0.71	0.68	0.71	0.67	Average 0.69	cc.
80° C	air	0.042	0.047	0.042	0.047	0.045	Average 0.045	cc.

be determined very well with this apparatus by filling with air instead of oxygen, though the oxygen pressure diminishes in the air during the test, but if the latter is not pushed too far, the resulting error is negligible. It will be seen from the above determinations that, with this mixture, the rate of oxidation in oxygen is 3.1 times greater than in air. Other tests have shown that this ratio is not the same for all rubber mixtures. As a rule this proportion, which cannot always be accurately determined, is somewhere between 2 and

3.5, so it may be said that the absorption of oxygen is roughly proportional to the square root of the oxygen pressure.

Table 2 gives the absorption of oxygen by some unvulcanized substances.

TABLE 2
ABSORPTION OF UNVULCANIZED SUBSTANCES AT 80° C

Crepe	0.007 cc.	Perbunan	0.015 cc.
Sheet	0.007 cc.	Neoprene-G	0.055 cc.
Crepe of low protein content	0.065 cc.	Pliofilm	0.000 cc.
Buna-S	0.018 cc.		
Gutta-percha	1st 15 minutes 1.8 cc.		
	2nd 15 minutes 2.2 cc.		
	3rd 15 minutes 3.4 cc.		
Gutta-percha + 2% phenyl-β-naphthylamine	0.025 cc.		
Gutta-percha + 2% benzidine	0.01 cc.		
Gutta-percha + 2% hydroquinone	0.005 cc.		

It shows clearly that raw rubber is very little oxidizable. Gutta-percha (unpurified) is very oxidizable, and becomes increasingly so when subjected to prolonged heating. The addition of an antioxygen is an exceedingly good deterrent to this oxidation. During the determination the gutta-percha is in a molten state, and one-half gram of this material is used per test.

Some rubber vulcanizates failed to produce proper check values when the same sample was tested twice, as the results obtained with Mixtures 2 and 3, given in Table 3, show.

TABLE 3
OXYGEN ABSORPTION DEPENDENT ON THE TIME OF OXIDATION AT 80° C

Mixture No. 2	1st determination 0.02 cc.	2nd test 0.007 cc.
Mixture No. 3	1st determination 0.04 cc.	2nd test 0.025 cc.

Mixture No. 2 was composed of Perbunan 100 parts, sulfur 1.5 parts, Vulkacite-AZ 1.8 parts, zinc oxide 5 parts, stearic acid 2 parts, phenyl-β-naphthylamine 1 part; vulcanized for 25 minutes at 142° C. The composition of mixture No. 3 was the same as that of No. 1 + 1 part of aldol.

As it was surmised that peroxides, destroyed by the thermal treatment, were responsible for this lack of reproducibility, the above mixtures were exposed for ten hours to the August sun, with the idea of promoting the formation of peroxides.

The results of the next oxidation determinations are given collectively in Table 4. The first determination was made one night after the exposure.

TABLE 4
THE EFFECT OF DURATION OF HEATING ON OXIDATION AT 80° C
AFTER PRELIMINARY EXPOSURE TO LIGHT

	1st Test	2nd Test	3rd Test
Mixture No. 1	0.40 cc.	0.32 cc.	0.15 cc.
Mixture No. 2	0.10 cc.	0.03 cc.	0.02 cc.
Mixture No. 3	0.06 cc.	0.045 cc.	0.04 cc.

The second determination was preceded by 3 hours' heating at 80° C, and the third by eight hours at 80° C, and, in addition, half an hour at 100° C. The results show that preliminary exposure affects oxidation very powerfully

indeed and that this effect is destroyed again by heating. These results thus confirm the investigations made by Morgan and Naunton[5], whose findings were somewhat similar.

SUMMARY

A modification of Dufraisse's oxygen absorption apparatus is described, with which it is possible to carry out the determination under constant pressure. As a result the oxygen absorption of rubber can be read directly in absolute terms, a secondary advantage being that the determination proceeds roughly four times as quickly as by the manometric method. Some results are given which show clearly, among other things, how considerable is the effect of preliminary exposure of the rubber to light on the oxidation.

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THE STATE OF POLYDISPERSION OF HEVEA LATEX.* I

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The rubber particles in the latex of *Hevea brasiliensis* are present in the form of a polydispersion, and their diameters lie within the range of 0.1 to 3 microns. The rubber hydrocarbon itself is composed of a mixture of macromolecules of different degrees of polymerization. Rubber latex is, therefore, a system which is at the same time both polydispersed and polymolecular.

It is well known that the degree of dispersion of a substance governs to a great extent certain properties of the substance. Moreover, astonishing as it may seem, in the great number of investigations which have been made of the composition and properties of latex and crude rubber, almost no attention has been paid to the part which may be played by the dimensions of the latex particles. However, in an investigation concerned with the centrifugation of latex, Loomis and Stump[1] have called attention to this possibility, and in a study of latex obtained by fractionation, and in which the majority of the latex particles were of large dimensions, McGavack[2] came to the conclusion that the protein content is proportional to the surface area of the globules.

This limited knowledge of the subject seemed to warrant a more thorough study of the problem, which is of fundamental importance both from the theoretical and practical points of view.

The investigation as a whole divided itself into three essential parts:

(1) separation of latex into fractions containing particles of different sizes, and measurement of the state of dispersion in these fractions,

(2) a study of the relation of these fractions to the composition of the rubber, *i.e.*, the relation between the content of nonrubber components and the size of the latex particles, and

(3) a study of the changes in the properties of the rubber hydrocarbon with change in the size of the latex particles.

The latex used in this investigation was ordinary latex, containing 38–40 per cent dry-rubber content and preserved with ammonia. For the most important points, a concentrated latex (creamed latex containing 60 per cent dry-rubber content) was also tested. These two latices were about two years old when the investigation was started, and they gave results which were in good agreement with each other. In the present paper, only the data obtained with the first of the two latices are presented.

FRACTIONATION AND DISPERSOIDAL ANALYSIS OF HEVEA LATEX

SEPARATION BY CENTRIFUGATION INTO FRACTIONS OF DIFFERING PARTICLE SIZES

When a polydispersed suspension is diluted and allowed to stand, it is found that, at the end of a certain time, under the influence of gravity, the

particles separate in the column of liquid, and that the extent of this separation depends entirely on their diameters. This process is represented schematically in Figure 1, in which for simplicity, only four different diameters of particles are shown. To make the representation still simpler, these four sizes of particles are grouped in four different columns. The right side of the diagram (Figure 1b) shows the distribution after a certain time of sedimentation. The concentration c in the different layers is a function of the height x of the liquid column, and the relation between these two factors can be expressed in the form of a sedimentation curve, or c/x curve. After a given time of sedimentation, there is a well defined concentration gradient in the polydispersed suspension. By dividing the column of liquid into four horizontal zones, according to the broken lines in Figure 1b, four fractions containing particles of different sizes are obtained. For the case represented in Figure 1, the fourth fraction is monodispersed. The zones above this lowest fraction are polydispersed, and the percentage by volume of the larger particles increases
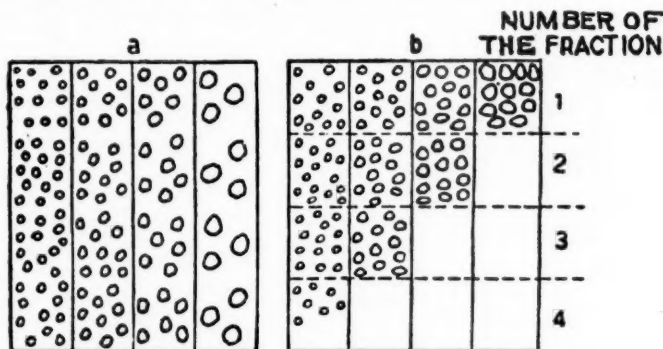
FIG. 1.—Schematic representation of the sedimentation of a suspension. *a*, before; *b*, after.

This principle was applied to the fractionation of *Hevea* latex. The dimensions of the particles of *Hevea* latex are so small that the velocity of sedimentation under the influence of gravity is very slow. Consequently this velocity was increased by resort to centrifuging. To this end a suspension centrifuge having four cups, with tubes of 230-cc. capacity, was used. The latex was centrifuged under such conditions that the c/x curve was an inclined straight line (this subject will be discussed later). The column of liquid in tube A was then fractionated carefully into several horizontal zones by means of the apparatus shown in Figure 2. The fractions thus obtained were transferred into flasks placed in the desiccator H.

Three variables must be considered in this centrifugation process: (1) the concentration of the latex; (2) the time of centrifugation, and (3) the number of turns of the centrifuge. With undisturbed sedimentation, it is possible, by means of these three factors, to calculate the compositions of fractions (3) and (4). However, under the actual operating conditions, sedimentation is disturbed by convection currents in fraction (4), set up not only by the more or less conical form of the receptacles but also by tangential forces and by the increase in temperature of the liquid. As a result it was impossible to carry out the fractionation in accordance with theoretical principles, and it has become necessary to operate on a purely empirical basis.

A general calculation, based on the velocity of sedimentation of a particle of spherical form in a centrifugal field, showed that centrifugation at a speed

of 2300 revolutions per minute for 60 minutes, in the absence of disturbing convection currents, gave a high concentration gradient in the column of liquid. Consequently these operating conditions were chosen for determining experimentally the c/x curves of a series of samples of latex of 5, 10, 15 and 20 per cent concentration, respectively. The contents of the centrifuge tubes were then fractionated. Estimation of the weight and percentage of rubber of each of these fractions made it possible to construct a graph showing the concentration c obtained as a function of the distance x of the level of the different fractions above the axis of the centrifuge.
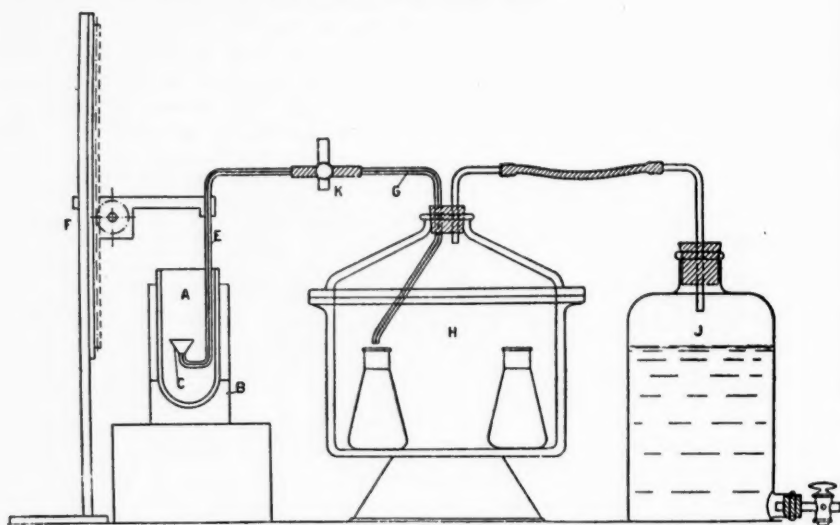
Fig. 2.—Apparatus for the fractionation of latex by centrifugation.

In this way the most regular c/x curve was obtained when the dilution of the latex corresponded to a rubber content of approximately 15 per cent.

After having established the different conditions to be used for centrifuging, a sample of latex sufficiently large for the various experiments was fractionated. The original latex was filtered, was brought to the desired dilution, and 0.3 per cent of ammonium oleate was added as a stabilizing agent. Fifteen series were carried out with 4-unit portions of 230 cc. Some data on these fractions are shown in Table I.

TABLE I

DATA ON THE FRACTIONATION OF LATEX

No. of fraction	Distance x on the axis (cm.)	Weight of fraction (grams)	Rubber content c (percentage)	Percentage of rubber, based on the total rubber	Specific gravity	Viscosity (centipoises)
1	7.9	0.675	67.0	21.1	0.940	paste
2	8.7	1.100	39.2	20.1	0.964	5.10
3	10.2	1.800	22.0	18.4	0.982	2.08
4	11.6	1.725	15.7	12.6	0.989	1.52
5	13.0	1.700	10.8	8.5	0.994	1.27
6	11.5	1.775	7.8	6.4	0.998	1.16
7	16.0	1.800	6.3	5.3	1.000	1.09
8	17.5	1.750	5.0	4.1	1.001	1.08
9	19.2	1.975	4.0	3.5	1.003	1.07
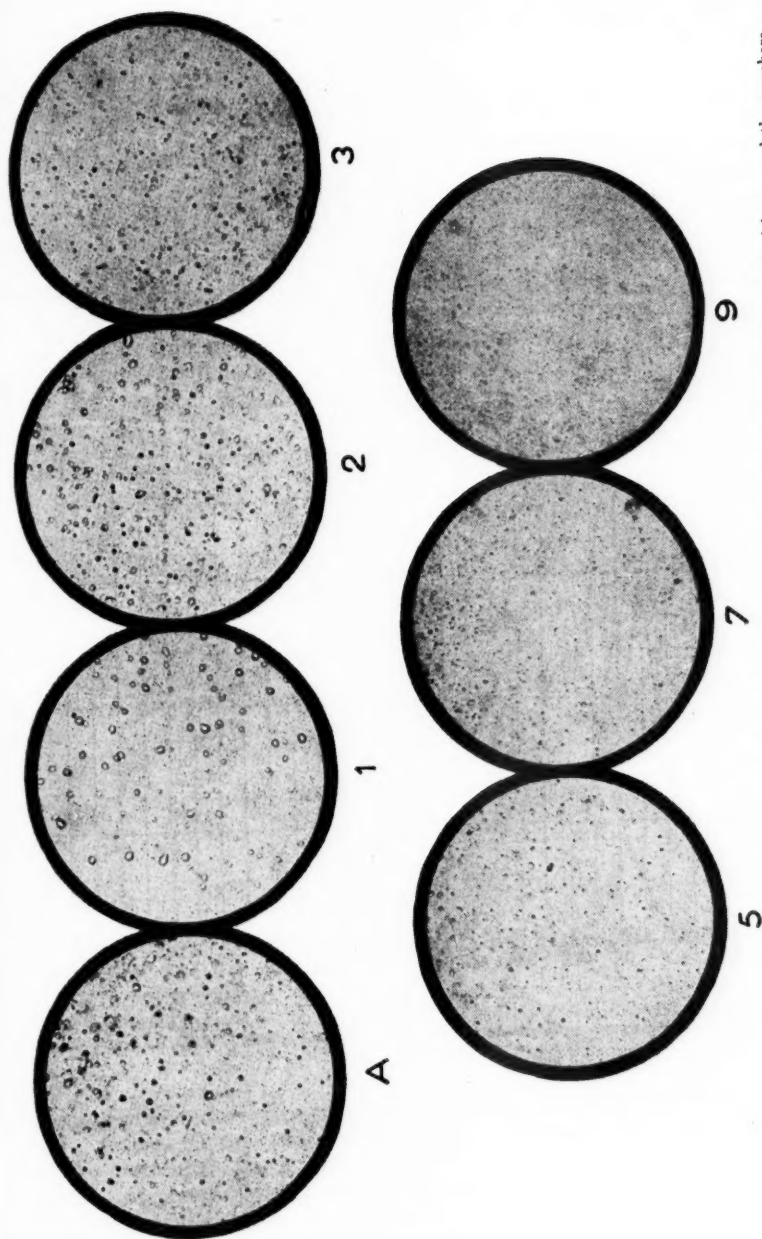
Fig. 3.—Photomicrographs of the original latex and of several fractions obtained from it. A represents the original latex, and the numbers under the various micrographs correspond to the numbers of the fractions.

DISPERSOIDAL ANALYSES OF THE FRACTIONS

The state of dispersion of the polydispersed fractions which were obtained can be determined very precisely by means of a distribution curve which shows the weight of the particles as a function of their diameter. For this purpose two methods were available, photomicrographic analysis and sedimentation analysis.

Photomicrographic analysis.—This method, developed by Green, has already been employed by Lucas and by McGavack in studying latex. Figure 3 shows photographs taken with an apochromatic objective N.A. 1.40, with a total magnification of 685. Special precautions were taken to obtain a sharpness sufficiently great for the negatives to be projected on a large scale and the diameters of the particles measured in millimeters. These photographs show that the desired fractionation was accomplished, since considerable differences in the sizes of the particles of the various fractions were manifest. Still better proof of this is to be had by an examination of the frequency-volume curves constructed from the photographic results (see Figure 4). Here $V(D)$ repre-
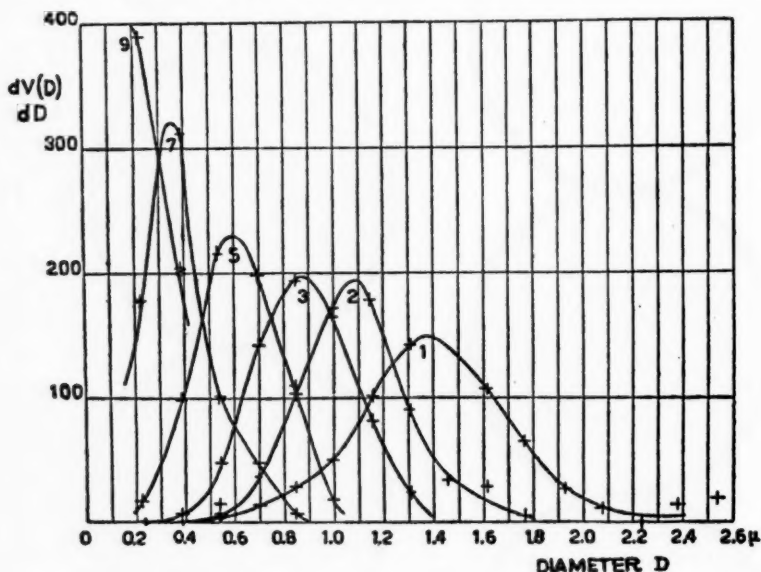
Fɪɢ. 4.—Frequency curves representing the volumes of various fractions of the original latex. determined by photomicrographic analysis.

sents the percentage by volume of the particles having diameters less than D.

The principle of the fractionation process is evident from Figure 4. Fraction 1, which contains the largest particles, contains at the same time particles of all diameters, and the base of its frequency curve extends through the complete range of diameters. On the contrary, the bases of the curves of the other fractions, which contained smaller particles are not so broad, and their peaks are displaced toward the left.

Actually the distribution curves obtained by this method of analysis (see Figure 5) do not give a completely true idea of the facts, particularly for the

fractions containing relatively small particles, because it is possible to detect and measure microscopically only particles with diameters greater than about 0.3μ, and the percentage of particles with diameters less than this value naturally increases with increase in the number of fractions. In addition, even with visible particles, photomicrographic analysis is not very precise and is very difficult to carry out. Accordingly recourse was had to another method to measure the degree of dispersion of the different fractions.
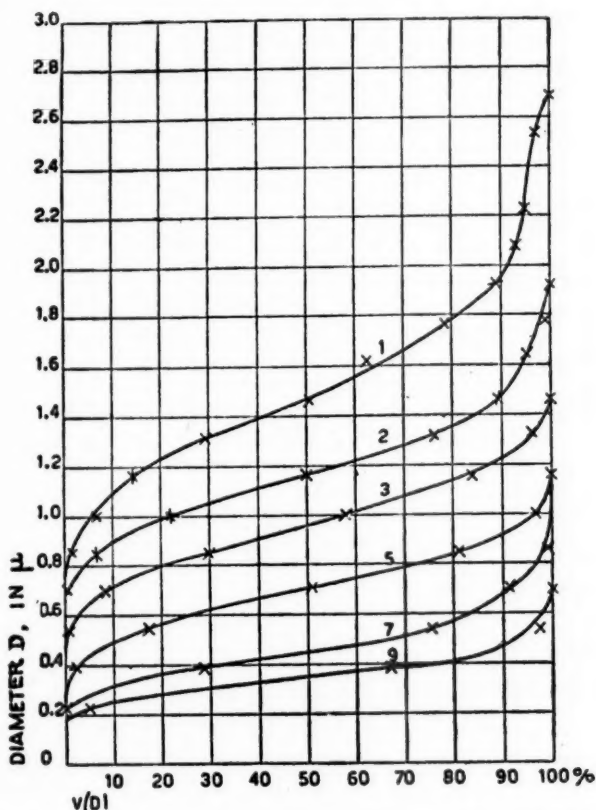
Fig. 5.—Distribution curves representing the volumes of various fractions of the original latex, determined by photomicrographic analysis.

Sedimentation analysis.—This method of analysis was used by Andreasen for studying mineral suspensions, and in the present work it was applied to rubber latex as a typical suspension, in which case the separation of the particles by gravity takes place very slowly.

This method of sedimentation analysis was used to obtain weight-distribution curves of several fractions. These are shown in Figure 6. Since the time of sedimentation did not exceed fourteen days, the experimental points represent only diameters greater than 0.4μ. However, in contrast to the difficulties encountered in photomicrographic analysis, the percentage of particles of relatively small diameters was known with sufficient precision to warrant extrapo-

lation of the curves to values of D lower than 0.4 μ (see the broken lines of Figure 6).

To obtain an overall comparison of the diameters of the particles in the different fractions, the diameter D 50 per cent, corresponding to a $V(D)$ value
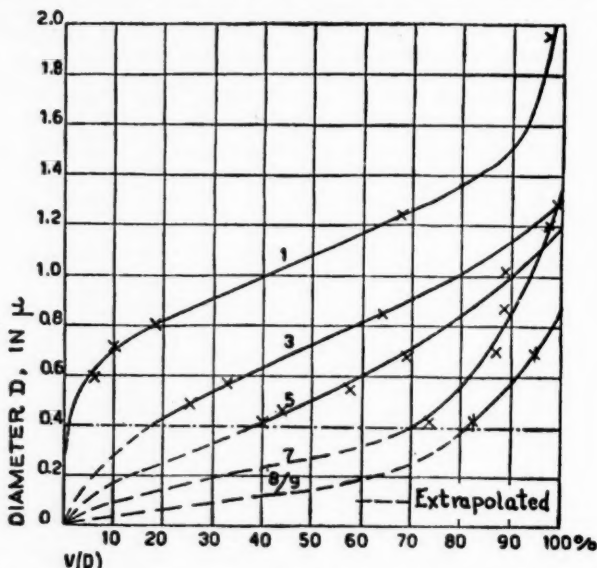
Fig. 6.—Distribution curves representing the weights of various fractions of the original latex, determined by sedimentation analysis.

of 50 per cent, can be utilized.   Figure 6 shows that the respective values of this factor are the following:

Fraction	1	3	5	7	(8+9)	original latex
D 50 per cent in μ	1.1	0.7	0.5	0.3	0.15	0.8

RELATIONS BETWEEN THE SIZE OF THE PARTICLES AND THE COMPOSITION OF HEVEA LATEX

It is well known that latex, which is a liquid of biological origin, shows at times considerable variations in composition as the result of biologic, climatologic and other influences.   These variations in composition appear not only in the rubber content of the latex but also in the percentages of nonrubber components, such as the proteins, sugars, lipides, cations and anions, which are bound to the rubber particles or are dissolved in the serum.   These variations in composition can likewise affect the properties of the rubber hydrocarbon.   It is these differences in composition which account for the variability in the properties of latex and crude rubber, a variability which is sometimes the cause of serious difficulties in processing these materials.   Only with a good theoretical knowledge of the composition of latex and of the factors which are capable of influencing the distribution of the nonrubber components in the dispersed phase and in the serum is it possible to solve this problem in a logical manner.   This is why a study of the relation between the size of the particles in latex and the content of nonrubber substances has proved to be particularly instructive.

The nonrubber components present in latex can be in solution in the serum or can be adsorbed reversibly on the surface of the rubber particles, or adsorbed irreversibly on the surface or, under some conditions, in the interior of the rubber particles.

When latex is washed thoroughly, the only nonrubber substances which remain are those which are adsorbed irreversibly.

In this case there is a simple relation between the size of the particles and the composition of the rubber, *viz.*, the percentage of adsorbed substances is always proportional to the total surface of the particles, at least under conditions where the thickness of the adsorbed layer is uniform. Since the total surface per unit weight is inversely proportional to the diameter of the particles, the smaller the latex particles, the higher must be the proportion of nonrubber substances on the rubber.

The various fractions, containing particles of increasing size, prepared as just mentioned, were purified in two successive steps.

The dialyzable substances, such as sugars, salts, nitrogenous compounds of low molecular weight, etc., were first of all eliminated with the aid of a dialyzer constructed especially for the purpose and a dilute ammoniacal solution. Following this, the dissolved colloidal substances, such as proteins and ammonium salts, were separated by precipitation by diluting the dialyzed latex to a rubber content of less than 5 per cent, adding a precipitating agent, then diluting strongly again, and treating a second time in the same way. It was calculated that, based on their content in the dry product obtained, the concentration of colloidal substances in solution after the second precipitation was not more than 0.01–0.02 per cent of their original concentration.

This purification was, moreover, as complete as it was possible to obtain, for a third precipitation did not lead to any further change in the composition of the rubber. It should be mentioned that the precipitation method was used because it is influenced to only a small degree by the size of the latex particles after centrifugation. Nevertheless, the precipitation process does have an influence on the results, for it was found that, under the same operating conditions, the smaller the size of the latex particles the lower was the yield from the precipitation. The loss of rubber by double precipitation was less than 1 per cent for fraction 1, whereas it reached approximately 20 per cent for fraction (8+9), the particles of which were the smallest.

After having purified in this way the different fractions by dialysis and double precipitation, the total content of dry substances in each was determined. Table II summarizes the results obtained.

TABLE II

COMPOSITION OF RUBBER PURIFIED FROM DIFFERENT FRACTIONS

Composition (percentage)	Fraction 1	Fraction 3	Fraction 6	Fraction 8+9	Original latex
Nitrogen	0.04	0.07	0.07	0.11	0.10
Ash	0.05	0.16	0.20	0.52	0.15
Aqueous extract*	0.5	1.0	1.2	1.7	0.6
Acetone extract	1.5	2.1	3.9	4.3	1.7
Fat acid (percentage of the acetone extract)†	0.7	1.2	2.4	2.7	0.7
Total nonrubber substances‡	2.3	3.7	5.7	7.2	3.3

* The aqueous extract contains, among other substances, 1-methylinositol, inorganic acids, nitrogenous compounds of low-molecular weight, and sugars. The extract was analyzed by the method of Dekker.
† Calculated as oleic acid according to the acid number of the acetone extract.
‡ The nitrogenous substances are considered to be proteins.

The data in Table II show that the major portion of the adsorbed non-rubber components is composed of lipides, half of which are fat acids. It should be noted that about one-quarter of the adsorbed substances were recovered in the acetone extract, whereas only a small part of the proteins and ash was removed by washing.

Since the average surface area of the particles per unit weight of rubber was known for each fraction, it was possible to determine whether the percentage of adsorbed substances was actually proportional to the total surface area of the particles. In each case an approximate idea of this was had by taking as a basis the value of the diameter D 50 per cent from the sedimentation analysis. It was then possible, with the different fractions, to compare the relative values of the surface area and the relative values of the nonrubber components by relating these values to those of fraction I taken as unity.

TABLE III

RELATION BETWEEN THE SURFACE AREA OF LATEX PARTICLES AND THE ADSORBED NONRUBBER COMPONENTS

Nonrubber components	Relative values for the fractions			
	1	3	6	8+9
Nitrogen	1.0	1.6	1.8	2.8
Ash	1.0	3.2	4.0	10.4
Aqueous extract	1.0	2.0	2.4	3.4
Acetone extract	1.0	1.4	2.6	2.9
Total nonrubber substances	1.0	1.6	2.5	3.1
Surface area of 1 gram of rubber	1.0	1.6	2.8	7.3

From Table III it is evident that, except for the ash content, the relative values of the different adsorbed substances in fractions 1, 3 and 6 approach those corresponding to the ratios of the surface areas of the latex particles. On the other hand, in the case of fraction (8+9) the values are definitely smaller. This may depend on the composition of the adsorption layer varying with the size of the latex particles; on the other hand, the values obtained are only approximately correct.

The question likewise arises whether the proteins adsorbed irreversibly on the rubber particles form a monomolecular layer. According to experiments by Gorter and Grendel, one milligram of protein spread out as a monomolecular layer covers a surface area of 1 square meter. For 1 gram of rubber, of density 0.91, dispersed as globules having a diameter equal to D μ, the surface area is:

$$\frac{\pi D^2}{0.91 \frac{\pi D^3}{6}} = \frac{6.6}{D} \text{ sq. meters}$$

Consequently 1 gram of rubber in fraction 1 has a surface area of 6.6/1.1 = 6.0 sq. meters; for a monomolecular layer of protein adsorbed on this surface, the protein content of the rubber would be 0.6 per cent. Now, according to Table II, this protein content is only $0.04 \times 6.25 = 0.25$ per cent; hence the rubber particles are not entirely enveloped by a layer of protein. Furthermore, it is evident from the data in Table III that, with decrease in the size of the particles, a progressively smaller part of their surfaces is covered with a layer of irreversibly adsorbed protein. This conclusion is in accord with that

drawn by Kemp and Twiss, from a study of the cataphoretic velocity of rubber particles, according to which the rubber particles in very dilute latex are only partially covered by proteins, while the remainder of the surface is composed of lipides. In addition to the latter, a certain quantity of ash and aqueous extract are present in this layer.

On the other hand it is possible that a small portion of these substances are also present in the interior of the rubber particles. Kemp reached the conclusion that if lipides were still present in rubber which he obtained from latex heated with an alkali, these lipides were not easily recoverable, and were present in the interior of the globules. It is possible to explain in the same way the fact that, even after extensive decomposition of the proteins, as for example, by heating latex with an alkali or in the presence of thermophilic bacteria, the final rubber which is obtained is not entirely free of proteins but contains 0.02–0.03 per cent of nitrogen.

Nothing definite is known about the percentage of substances adsorbed reversibly, although in a general way this percentage must depend on the concentration of the serum and diminish with increase in the dilution of the latex.

The relation between the size of latex particles and the substances dissolved in the serum was studied by comparing, for each fraction, the analyses of rubber obtained by evaporation (designated by TS as the total solid substances) and by coagulation (designated by DRC as the dry rubber content).

The data obtained are given in Table IV.

TABLE IV

Fraction	NH₃ (percentage)	DRC	TS	TS/DRC	Percentage nitrogen		Percentage ash		Percentage aqueous extract		Percentage acetone extract*	
					TS	DRC	TS	DRC	TS	DRC	TS	DRC
1	0.07	67.0	67.7	1.01	0.07	0.04	0.17	0.06	1.2	0.5	2.4	2.2
2	0.13	39.2	40.4	1.03								
3	0.18	22.0	23.4	1.06	0.44	0.17	0.72	0.08	4.2	0.7	3.8	3.7
4	0.20	15.7	16.8	1.07								
5	0.21	10.8	11.8	1.10	0.92	0.44	1.33	9.10	13.1	1.7	6.4	6.1
6	0.22	7.8	9.2	1.17								
7	0.23	6.3	7.6	1.20	1.57	0.74	2.12	0.17	20.4	3.3	8.6	8.9
8	0.24	5.0	6.5	1.28								
9	0.24	4.0	5.5	1.37	2.16	1.46	3.31	0.38	25.9	12.0	12.1	12.9
Original latex	0.22	15.7	17.0	1.08	0.59	0.30	0.89	0.10	7.3	1.5	4.4	4.5

* These values are somewhat higher than those for normal latex because ammonium oleate was added as a stabilizing agent.

Whereas in the case of purified rubber the percentage of nonrubber components increases relatively little with decrease in the size of the latex particles, in the case of rubber which has not been purified (whether prepared by evaporation or coagulation) this increase is very large, and is related only indirectly to the size of the particles. It is evident from the values in the third and fourth columns of Table IV that the rubber contents of the various fractions decreased greatly with decrease in the size of particles. Consequently, in the case of fractions with relatively small particles, there is a definite increase in the content of serum substances with respect to the rubber present. This is what is expressed by the ratio TS/DRC, and which explains also the considerable increase in the content of nonrubber components in the evaporated samples.

In the coagulation of latex by acetic acid, the noncoagulable substances are removed by washing, but the content of coagulable substances, notably

proteins and lipides, increases greatly in the dry rubber with decrease in the size of the latex particles, for the same reason as that pointed out for the total solids.

It can be concluded from these results that, in the fractionation of latex by centrifuging, the size of the particles is the only factor which governs either directly or indirectly, the composition of the resulting rubber. Fractions with relatively small particles always have lower rubber contents than fractions with relatively large particles; hence they possess, per unit weight of rubber, not only a greater surface area of their particles, but also a higher percentage of substances dissolved in the serum.

THE MORPHOLOGY OF RUBBER LATEX PARTICLES
A CRITICAL REVIEW *

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The morphology of the hydrocarbon particles of latices obtained from several rubber producing plants has in recent years again been the subject of studies applying the most modern tools of research. Lucas[1] used for his studies an ultraviolet light microscope and later ultramicrocinematography[2]. Quite recently Hendricks, Wildman, and McMurdie[3] applied electron microscopy for the first time for this purpose.

Since some of the deductions in regard to the form and structure of latex particles which have been drawn from these studies differ in several respects from conclusions based on micrugic and ultramicroscopic studies, some of which were reported twenty years ago[4], it seems advisable to clarify the picture. Such clarification is most important at present, because a better knowledge of the morphology of natural and synthetic rubber latex particles might offer a valuable aid in explaining some of the differences in the properties of these hydrocarbon polymers, which are not readily explainable on the basis of differences in chemical composition alone.

COMMENTS ON EXPERIMENTAL METHODS

On the basis of his studies, Lucas[5] came to the conclusion that the particles of *Hevea* latex are all small spheres and that the larger particles are formed only by several small particles being merged into one, and that the egg-shaped particles referred to in previous publications[6] are not individual particles, but the result of aggregation of several small spherical particles. The same opinion is also expressed by Hendricks and his collaborators, who base it on their electron microphotographs[3].

However, if one takes the colloid chemistry of rubber latex into consideration, these deductions are not conclusive. Lucas adds a solution of sodium chloride to the latex to stop the Brownian motion of the rubber particles before he makes the slide for his microscopic observations. He thereby reduces the zeta- or electrokinetic potential of the particles. Agglomeration results from such treatment. That primarily pearlstringlike aggregation and not cluster formation results from the addition of a concentration of monovalent counterions as used by Lucas has been pointed out and explained by several scientists[7]. That drying of a diluted latex, necessary when preparing a specimen for the electron microscope, also results in aggregation or change of the shape of the particle was also reported long ago[6]. Besides this, the latex used in these ultraviolet and electron microscope studies was either preserved with ammonia[5] or not fresh[3]. Natural rubber latex is a very unstable colloidal sol, and unless the morphological studies are carried out with latex on the plantation and immediately after tapping, the results do not permit drawing conclusions about the morphology of the latex particle as it exists in the plant[8].

That the egg- or pear-shaped particles in fresh *Hevea* latex are not the result of aggregation of small spherical particles has been shown not only by studying fresh latex particles microscopically with transmitted light after they had been embedded in a gelatinous dye which prevents aggregation and complete dehydration[6], but also by the use of an ultramicroscope[9] and by ultramicroscopic motion pictures of fresh latex[10]. The fact that fresh latex from given trees contains particles having a shape characteristic of the individual tree also speaks against the assumption that egg- or pear-shaped particles are the result of agglomeration[10]. It certainly would be a miracle if a given tree would always produce a latex, the particles of which agglomerate in just such a way that they always give the same shape and size of the agglomerate.

In the case of *Funtumia elastica*, the drawbacks of the technique used in preparing electron-microscope slides are even more evident. In the latex the particles are perfect spheres and not irregular. That this latex is a true emulsion has been clearly demonstrated by the use of the micromanipulator[8]. The same criticism holds for the latex of *Manihot Glaciovii*. Freundlich and Hauser[8] admittedly did not mention the presence of very small spherical particles, but their ultramicroscopic pictures and the results of micromanipulation indicate clearly that the rod-shaped particles of fresh latex are not agglomerates.

STRUCTURE OF HEVEA LATEX PARTICLES

That the protein adsorbed on the surface of the *Hevea* latex particle[11] is not responsible for the nonspherical shape has been demonstrated by studying the shape of particles from latex which has been deproteinized, either by supercentrifuging it or by trypsin digestion[8]. Such treatment does not affect the shape. Furthermore it has been demonstrated, by the use of a micromanipulator, that the surface of the *Hevea* latex particle is composed of a very elastic substance that is not affected by chemicals which destroy proteins, whereas the inside is composed of a liquid of honeylike consistency. That the outer shell of the latex particle must be composed of the hydrocarbon in a higher degree of polymerization than the inside has been clearly demonstrated by studying the effect of solvents which were introduced into the particles with micropipettes[6]. The change in the morphology of the various latex particles upon vulcanization is also significant[8]. All these experimental results indicate that the structure of *Hevea* latex particles, as postulated by Freundlich and Hauser[6] and later more fully by Kemp[12], is based on sound evidence.

Hendricks and his collaborators[3] state that, while this concept is simple, there is a serious argument against it: namely, a mechanism for separation of two fractions of rubber in latex is implied. This point of view must be based on a misinterpretation of the paper by Freundlich and Hauser[8], who twenty years ago expressed the same opinion in regard to the composition of the hydrocarbon part of the latex particles as Hendricks and his coworkers have now postulated. The correct translation of the pertinent passage in the paper by Freundlich and Hauser reads as follows:

". . . the interior of the particle is a sol, the dispersion medium being rubber hydrocarbon, while its polymerized form is present as the dispersed phase in the particles. On the surface the sol has set to a gel, in which the polymerized phase is predominant. Cases are known in which hydrocarbons are present in such a dual condition, as, for example, the relation between styrene and gelatinous metastyrene. . . ."

IMPORTANCE OF MORPHOLOGICAL STUDIES

The results of these microdisections and microchemical studies are well in line with the differences in properties exhibited by the rubbers obtained from these latices and, therefore, the morphology of the latex particles, as revealed by the micromanipulator technique, deserves more attention in our attempt to produce a truly synthetic rubber, because the development of the synthetic rubber industry and the still undeniable fact that GR-S (Buna-S) differs in many respects from natural rubber offer a further substantiation for the above-described structure of natural rubber. Micrurgic studies of GR-S latex particles, details of which will be published shortly, reveal that the particle is of uniform composition corresponding more to the gel than the sol fraction of natural rubber. These tests seem to indicate also that not all of the particles of the emulsion are composed of the copolymer, but that the emission also contains pure polystyrene and polybutadiene particles. These differences in the morphology of the latex particles, therefore, may offer a better explanation for the differences of the rubbers obtained therefrom than just the difference in the composition of the molecule.

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PROCEDURE FOR DETERMINING PHYSICAL PROPERTIES OF FILMS FROM GR-S LATICES *

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This article describes a new procedure for determining the physical properties of films from GR-S type of synthetic rubber latices. To obtain satisfactory films for testing, the latex solids should be above 30 per cent. A suitable formulation which will reach the optimum cure in from 30 to 60 minutes at 100° C is as follows:

Polymer	100.0
Sulfur	2.0
Zinc oxide	3.0
Zinc mercaptobenzothiazole	1.5
Zinc dibutyldithiocarbamate	0.5

If zinc mercaptobenzothiazole is to be omitted, it is desirable to increase the dithiocarbamate to about 1.0 part. If the dithiocarbamate is not used, vulcanization should be carried out at higher temperatures, *e.g.*, 120° C. These vulcanizing ingredients may be used as a composite dispersion by ball-milling the accelerator, sulfur and zinc oxide with 0.5 parts dispersing agent, such as Daxad-11, Vultramine, etc., to give a 45 to 50 per cent dispersion.

It is recommended that freshly prepared pastes be used, since experience has shown that erratic results may be obtained when old pastes are used, particularly those containing zinc oxide. Additional stabilizers, such as soap, may be used with this compound if required in some cases. Films should be prepared promptly after the compound is made, for prevulcanization may occur in the final films and produce erratic results.

PREPARATION OF FILMS

Dispersions of the vulcanizing ingredients or mixture should be stirred into the latex carefully to avoid incorporating air. Air in the compound may show in the film as bubbles, and cause erratic results. It is, therefore, advisable to allow the compound to stand for some time (1 to 2 hours) after mixing to allow the air to escape. It is frequently common practice to subject the compound to a mild vacuum (20 to 25 inches of mercury) to hasten the removal of air before depositing the films.

Since most latices are evaluated at relatively low solids, cracking of films frequently occurs on drying, due to marked shrinkage. To avoid this, it is desirable to increase the viscosity of the mix considerably, *e.g.*, by adding such thickeners as ammonium alginate from 0.25 to 0.5 parts per 100 parts polymer, alkaline casein solutions, etc. The optimum amount depends on the choice of thickener and the solids of the latex. The viscosity usually desired is approximately 75 to 100 cps.

Films are spread on smooth clean glass plates (Figure 1), held in the horizontal plane and about 10×12 inches in size, by means of a spreader bar. This latter device is simply a straight bar of metal which has been cut along one edge to give a uniform depression of about 0.04 to 0.05 inches in depth. When latex is spread with such a bar, the wet film thickness is about 0.02 inches thick, providing the compound is at 40.0 per cent solids concentration.
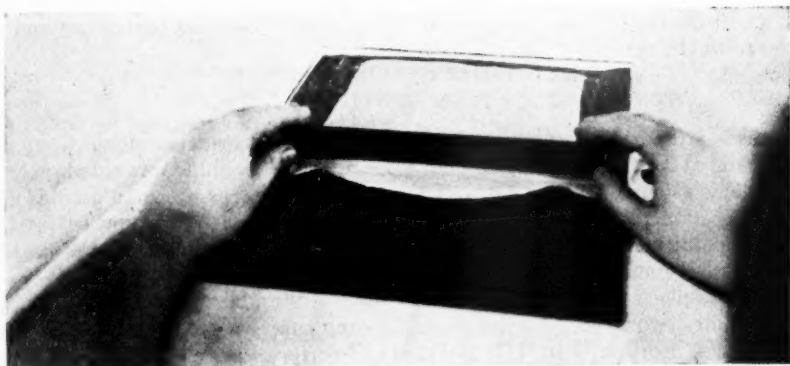
FIG. 1.—Spreading films on smooth, clean glass plates. Note that the spreader bar is cut along one edge to give a uniform depression of 0.04 to 0.05 inches in depth.

Films are usually dried in air overnight at room temperature, although accelerated drying at elevated temperature may be used. The maximum température to avoid precure should not exceed 50° C. After drying, the upper surface is dusted with a fine powder, such as soapstone, mica, whiting, etc., and the film is stripped from the plate (Figure 2), following which the
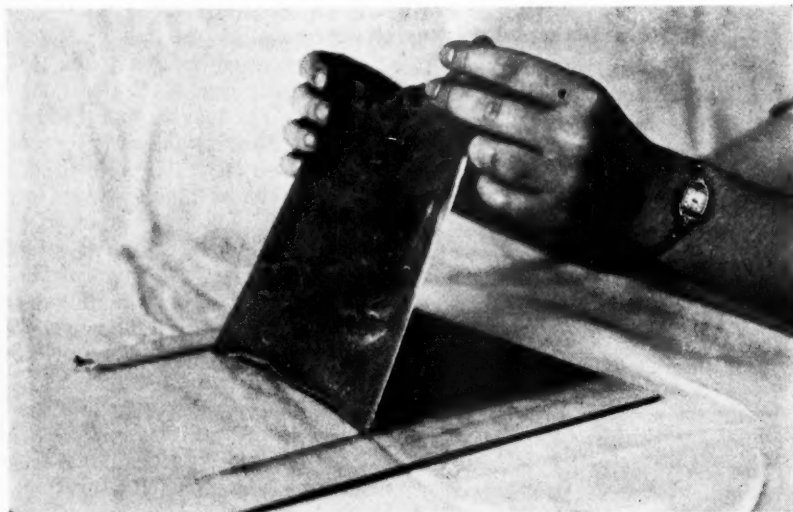
FIG. 2.—Stripping the film from the plate. After stripping the film is divided into four pieces of equal size for testing purposes.

reverse side of the film is similarly dusted. The film is then divided into four pieces of equal size for testing.

VULCANIZATION

Vulcanization is conveniently carried out by suspending films in an air oven, with efficient circulation of the air. The formula given above will give optimum cures in 30 to 60 minutes at 100° C. A range of cures is usually run, such as 15–30–60–120 minutes at 100° C, to include both an undercure and an overcure in the series.

FILM TESTING

Tensile strength, modulus or stress at 300 per cent or other elongation, and elongation at break are determined with a Scott machine provided with a special head (such as Model No. L-3 SP), recording forces up to 10 pounds and separating at a rate of 20 inches per minute. Permanent tension set at the breaking point is measured by determining the increase in length of the broken specimen (between bench marks) one minute after break.

The test-piece is cut from the stock with a standard $\frac{1}{8} \times \frac{1}{2}''$ dumbbell die. Usually two to six tests are made for each cure. The A.S.T.M. Standard Section, 1942 Edition, Part III, D-412–41, describes formulas and calculations for such rubber-film testing.

In comparing different latices, it is often desirable to average all the results for the range of cures, and to consider these averaged values as characteristic of the latex, rather than to give only the data for the optimum cure.

EXTRACTION OF RUBBER FROM
CRYPTOSTEGIA GRANDIFLORA *

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In an earlier communication[1] on the subject, it was stated that an improved method for the extraction of rubber from harvested partially dry twigs of *Cryptostegia grandiflora*, which has assumed considerable importance as a secondary source of rubber, has been worked out in these laboratories. The facts that (1) its latex is distributed throughout the plant (unlike *Hevea*, in which the latex cells are localized in a definite region in the cortex), and (2) its latex does not ooze out in a continuous stream, but coagulates very soon at the cut surface, rendered it necessary to develop either a modified tapping technique involving decapitation of shoots and collection of "plugs," or a process in which the entire plant or the harvested shoots are suitably treated to release their rubber. The Rubber Directorate, it is understood, are experimenting with modified tapping methods, which have proved to be somewhat cumbersome and uneconomical. At the instance of the Supply Department, investigations were undertaken in these laboratories to develop a more convenient and economical process for the extraction of rubber from the plant.

Some of the commercial processes involving the treatment of the whole plant which are in use for extracting rubber from *Parthenium argentatum* (Guayule), Kok-saghyz (Russian dandelion), Tau-saghyz, milkweed, etc., are grinding the material in successive stages with different amounts of water[2]; subjecting the material to increasing pressure, which is then suddenly released to disrupt the cells[3]; enrichment of the material by mechanical (especially by diffusion), and microbiological methods, and then recovering rubber by centrifuging[4]; froth-flotation[5]; mechanical crushing followed by flotation and fermentation[6]; and solvent extraction of finely ground leaves under pressure[7]. Regarding *C. grandiflora* itself, Viswanath[8] found that by treating the finely ground plant material with steam under pressure, with or without preliminary hydrolysis, rubber could be released and collected. The following percentages of recovery were reported: 0.96 from central pith, 0.07 from bark and 0.19 from tender twigs. Mechanical grinding followed by flotation has also been tried[9]. A review of the various methods employed has been given by Fennel[10].

In these laboratories, it has been found that the average rubber content of the harvested shoots divested of leaves is 0.3–0.5 per cent, while it varies between 0.6 and 2.0 per cent in leaves. The process worked out for the treatment of twigs, after a series of trials, consists of the following stages: preliminary digestion of the harvested, partially dry, chopped twigs with boiling sodium hydroxide solution (0.3–0.4 per cent) for 4 hours; washing the boiled material; adjusting its pH to 9.0–9.5; ball-milling for 3 hours; washing the ground material out of the mill, and stirring it in about 10 times its volume of water; and screening off the worms of rubber that float to the surface.

193

EXPERIMENTAL

The weights of the twig material used in the experiments varied from 60 grams to 1 kilogram. Many of the results obtained in the small-scale experiments were repeated on a large-scale with 1-kilogram lots, and the results reported in this paper have been repeatedly confirmed. For the sake of uniformity all the results that follow are given on the basis of 1-kilogram lots of experimental material. For small-scale work a ¾-gallon ball-mill was used, filled with 110 iron balls of 4/5-inch diameter, rotating at 57 r.p.m. For large-scale work a 4-gallon ball-mill was used, filled with 6 iron balls of 2.5-inch diameter and 50 balls of 4/5-inch diameter and rotating at 86 r.p.m.

The plant material was dried for two days and defoliated, and the leaf-free twigs were chopped to small bits. A representative sample of each batch of material was taken for the determination of rubber content by solvent extraction.

Determination of rubber content.—A weighed amount of the chopped material was dried in a steam oven for 6 hours, reweighed, and then extracted with carbon tetrachloride for 8 hours. The solvent was distilled off from the extract, the residue extracted for 8 hours with acetone, and dried to constant weight. This gives the actual rubber content of the material.

Yield and recovery.—In the results given below, yield refers to the weight of the dry, crude rubber, that floats to the surface when the disintegrated plant material is stirred up with water. For calculating recovery, the rubber hydrocarbon content of the crude material was determined by extraction with carbon tetrachloride and precipitation by excess of acetone. The rubber that separated out was dried and weighed.

In the process worked out, the factors that can influence the efficiency of extraction are: (1) strength of the cooking alkali; (2) duration of cooking;

TABLE I

EXPERIMENTAL CONDITIONS FOR STUDYING THE EFFECT OF VARYING THE FACTORS ON YIELD OF RUBBER

Series No.	Concentration of alkali solution (percentage)	Duration of cooking (hours)	Duration of keeping (hours)	pH* of the mill charge	Concentration of the mill charge	Duration of milling (hours)
1	Varied from 0 to 2.0	2.5	42–48	9.0–9.5	Hand pressed pulp + ⅓ its weight of water	2.5
2	1.0	Varied from 0 to 5	42–48	9.0–9.5	Same	2.5
3	1.0	2.5	Varied from 0 to 92	9.0–9.5	Same	2.5
4	0.5	4.0	24	Varied from <3.0 to >11.0	Same	2.5
5	0.5	4.0	24	9.0–9.5	Varied by adding dilute alkali (pH 9.0–9.5) to hand-pressed pulp 0 to 16 liters	2.5
6	0.5	4.0	24	9.0–9.5	Pressed pulp + ⅓ its weight of water	Varied from 0.5 to 6

* Determined by B. D. H. Universal Indicator

(3) duration of keeping the cooked material; (4) pH of the mill charge; (5) concentration of the mill charge; and (6) duration of milling. A systematic investigation of these factors was undertaken to determine the optimum conditions for the extraction of rubber.

By varying one of the factors, while keeping others constant, the optimum for that factor could be ascertained. The experimental conditions are set down in Table I, and the results obtained are represented graphically in Figures 1 to 6.
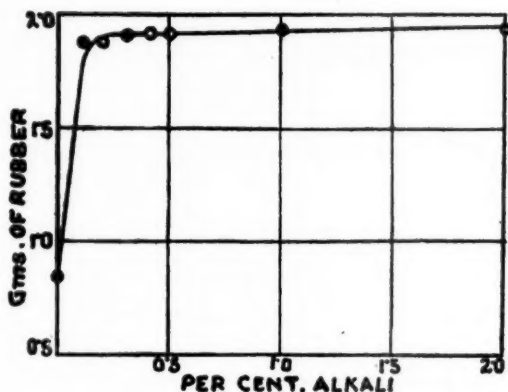
FIG. 1.—Effect of varying the strength of alkali on yield.
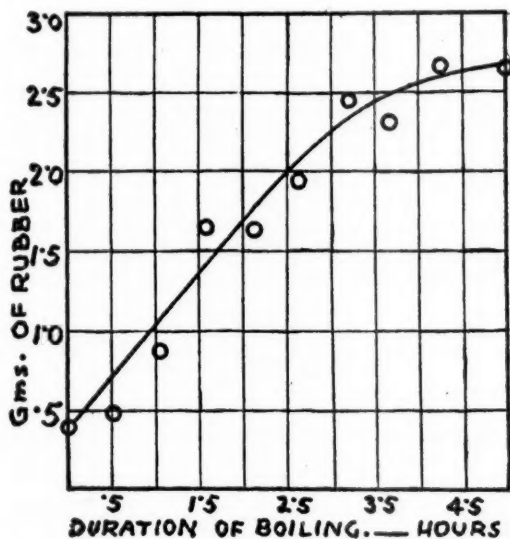
FIG. 2.—Effect of varying the duration of cooking on yield.

The effect of varying at random the strength of cooking liquor, duration of cooking, and period of storage of cooked pulp is shown in Table II. The pH of the mill charge was 9.0–9.5, and the milling period was 2.5 hours.
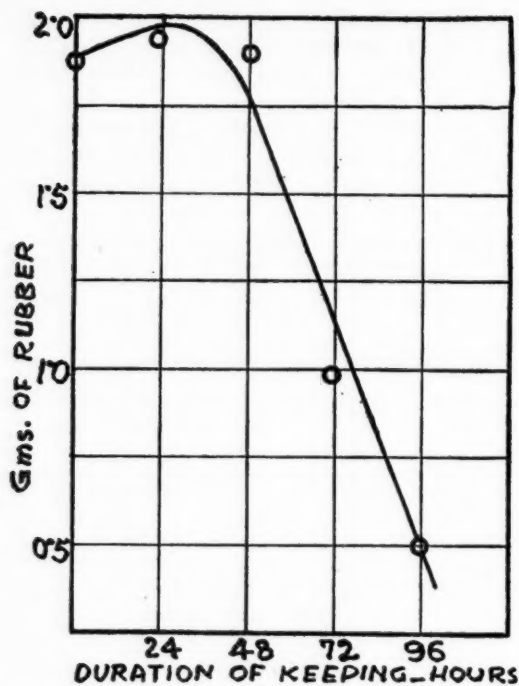
FIG. 3.—Effect of varying the duration of keeping on yield.
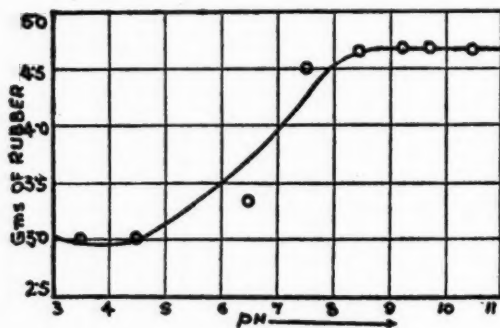
FIG. 4.—Effect of varying the pH of mill charge on yield.
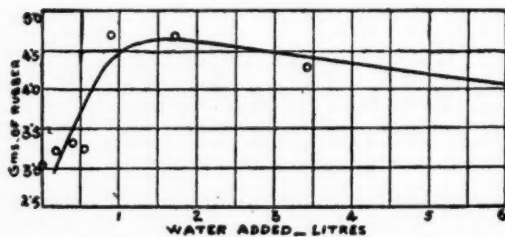
FIG. 5.—Effect of varying the concentration of mill charge on yield.
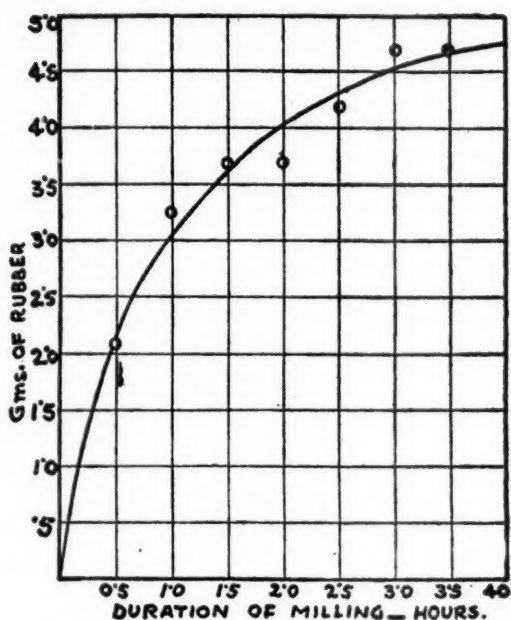
Fig. 6.—Effect of varying the duration of milling on yield.

TABLE II

No.	Concentration of NaOH solution (percentage)	Duration of cooking (hours)	Duration of keeping (hours)	Yield (grams)	Actual rubber content (grams)
1	0.3	4	24	2.82	3.33
2	0.5	4	24	2.66	3.33
3	2.0	4.5	36	2.66	3.33
4	1.5	3	70	0.50	3.33

The process was applied to three types of experimental material obtained through the courtesy of the Supply Department. The yields are given in Table III.

TABLE III

Description of material	True rubber content (grams)	Yield (grams)	Recovery (percentage)
1. Whole plant	3.5	2.5*	71.4
2. New shoots from old bushes	4.5	4.0	88.9
3. Mixed prunings from old bushes	4.6	2.5	54.3

* The rubber particles sank down into water having engulfed wood particles.

DISCUSSION

It will be seen from the values given above that the optimum conditions for the alkali strength, duration of cooking and period of storage of the cooked pulp are, respectively, 0.3 per cent, 3–4 hours, and 24 hours, respectively. From Figure 4 it is clear that pH of the pulp during disintegration in the

ball-mill profoundly influences the yield.   Thus, while some quantity of rubber is obtained at all values of pH, the maximum yield is secured when the pH range is 7.0–10.5.   The pH also influences the quality of rubber.   When the pH was low, that is, when the pulp was disintegrated under highly acidic conditions, a dark colored product was obtained which was weak in texture. In the highly alkaline range (greater than 10.5), the rubber was somewhat lighter in shade, but it was also weak.   The best product was obtained when the pH lay between 9.0 and 10.0.   The color of the product was considerably improved when 0.01–0.05 per cent of p-phenylenediamine was added to the charge before milling.

About 10 per cent of the plant material remained uncrushed under the best conditions secured in these studies.   Quantitative recoveries were, therefore, not possible.   The best yields were secured from newly harvested shoots from old bushes of *Cryptostegia*.

The pulp obtained as a byproduct after removal of the rubber is likely to find use in the manufacture of pressed boards.   This possibility is being examined.

The rubber obtained by this process is tough.   It is almost colorless when fresh, but turns somewhat dark on storage.

Arrangements are being made to apply the process on a commercial scale and to work out the costs.

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ADHESION OF RUBBER TO BRASS PLATE *

W. A. GURNEY

Introduction.—The brass-plating process is one of the most important methods of bonding rubber to metal. It consists of depositing a thin layer of copper zinc alloy on the surface of the metal. The rubber is then moulded in contact with the brass deposit, and in most cases, a strong bond is established during vulcanization.

Even, however, when all precautions are taken, bond failures occur, often with no obvious cause, so the process is still somewhat suspect. It is only fair to say, however, that this variability appears to be common to most methods of bonding rubber to metal, and that in general production a high level of adhesion is maintained.

Primary factors of bonding.—There can be little doubt that the bond between rubber and brass plate is the result of a chemical interaction between them. In all cases when a bond of any kind is obtained, the brass is discolored. It is also significant that most metals that have been used for direct adhesion to rubber, such as copper, brass, cobalt and monel, are materials which are known to cause rapid deterioration of raw rubber. On the assumption that sulfur is necessary for adhesion, the bond is generally throught to depend on a sulfide interlayer.

Whatever the actual adhesive may be, it is produced by chemical action and, therefore, the fundamental factors affecting the bond are only three. These are the properties of the two reactants and the conditions of the reaction. In the case under consideration the factors may be denoted as the activity of the rubber, the activity of the brass, and the condition of the vulcanization process during which the bond is formed. It is proposed to discuss these factors in this paper.

Experimental procedure.—Most of the experiments on which this paper is based were made with compounds of a general type containing rubber 100, channel black 40 to 60, zinc oxide 5, sulfur 3, stearic acid 3, and accelerator (usually mercaptobenzothiazole) $\frac{1}{2}$–1 parts. The brass plating was obtained from production baths which were in regular use.

As the three primary factors are themselves complex, it is difficult to maintain conditions sufficiently uniform over a long period to avoid results which do not apparently contradict one another, and for this reason it was found desirable to design experiments to cover a wide number of variables, and to make each experiment complete in itself. Many were designed as factorial experiments, as described by Fisher[1], with the object of covering as wide a field as possible. In particular, if different brasses were being examined at one time they were preferably moulded in the same mould with the various rubbers laid across them in strips. If different cures were being tested the samples for all were plated at the same time. This avoids the confusing results which can be obtained if rubbers are moulded at various times to unspecified brass plate.

It may be useful also to discuss the methods of testing adhesion.   There are two general methods. The first depends on breaking the bond by a direct pull, either in tension or shear, and the second method involves tearing a strip of rubber from the bonded surface.

The first method is recommended by the American Society for Testing Materials[2], and has been used by Yerzley[3] and Buchan[4].   It has the advantage of giving bond strengths as load per unit area and is, therefore, essential as a basis for design.   Unfortunately the variability of the test is high, and a number of test pieces must be broken to obtain a representative value.

The second method, the tear-down test, is not suitable for quantitative work, owing to the wide variation of tearing loads in any one test[5], and the figures are of no use for design, but the simplicity of preparation of samples makes the method attractive for exploratory research and for control testing. Both methods have been used in the experiments described in this paper.

First factor: The compound.—The effect of the compound may be considered as made up of two components, the actual ingredients and the physical state of the stock.

Of the chief ingredients of a rubber compound, softeners and antioxidants do not appear to have a pronounced effect on bond[4].   Stearic acid, although harmful in some bonding processes, has not been found to affect rubber bonding up to 5 per cent.

The effect of reinforcing fillers has been discussed by the author[6] and by Buchan[4].   Unloaded pure-gum mixings have an adhesion about 200 lbs. per sq. inch, but the addition of reinforcing blacks rapidly raises this, so that with 30 parts of black per 100 rubber adhesions of 1000 lbs. per sq. inch can be reached.   If an adhesive layer is assumed to be formed, this increase may be due to a rise in the tensile strength of the interlayer, as found by McBain and Hopkins[7] for glues.

Sulfur is apparently essential to the bond, for mixings vulcanized without sulfur by means of thiurams or nitrobenzene do not adhere to brass plate. Excellent adhesions have, however, been obtained with as little as $\frac{1}{2}$ part of sulfur per 100 of rubber, and although the adhesion rises with increasing sulfur, it does so only slightly.

The ingredient which seems to have the most pronounced affect on bond is the accelerator.   Generally, but by no means always, high acceleration diminishes the bond, as shown in Figure 1.

A visual demonstration is given in Figure 2.   This is a photograph of a plate on which alternate layers of similar compounds with high and low contents of mercaptobenzothiazole (MBT) were moulded side by side.   The areas with $1\frac{3}{4}$ and 2 per cent MBT have not bonded, whereas with $\frac{1}{4}$ and $\frac{1}{2}$ per cent MBT the bond is excellent.

The results of Buchan[4] show, although he did not consider variations in quantity, that with increasing activity of the accelerator, the adhesion strength falls.

A similar result is obtained with different raw rubbers.   Table 1 shows the comparison between adhesion strengths and scorching from compounds pre-

TABLE 1

Sample No.	2	3	4	1	6	8	7	5
Adhesion (lbs. per sq. in.)	1067	1043	871	868	181	796	658	605
Percentage Recovery (scorching)	8	8	8	12	13	13	13	83

pared as nearly alike as possible from eight different raw rubbers. The scorching is the percentage recovery after 30 minutes at 115° C, measured by a Williams plastometer. There is a high correlation between scorching and adhesion strength.

It seems, therefore, that the rate of vulcanization of the stock is a most important factor in brass-plate bonding, and that an increase in vulcanization activity is accompanied by a decrease in activity of the bonding reaction, as demonstrated by Figure 1. In other words, vulcanization of the rubber and formation of a bond to the brass are in opposition, a most important point.
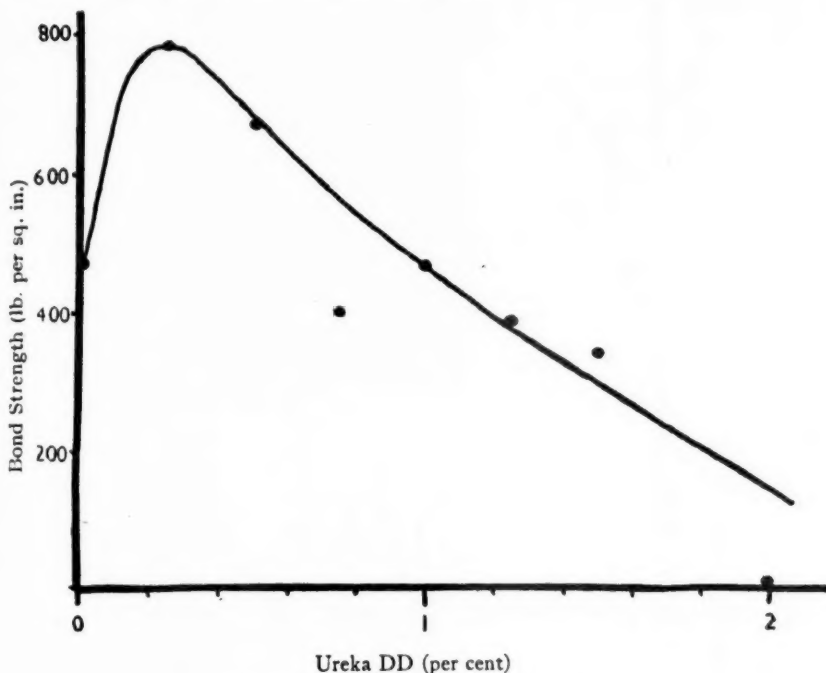
Fig. 1.—Effect of accelerator content on bond

It must be emphasized, however, that low acceleration does not necessarily give a good bond. Other factors are involved, as will be shown later.

The physical condition of the rubber does not appear to have a large effect on the bond. In one experiment, a rubber compound was remilled for periods ranging from 5 to 90 minutes on a warm mill, and no difference was found in the adhesion. Buchan[4] has reported similar results. It has, however, to be considered that the plasticity of the stock influences the behavior during moulding, and thus may have a secondary effect on the bond.

Second factor: The brass.—There appear to be three components of this factor, the composition of the brass, the atomic arrangement (crystal structure) and the presence of adsorbed or codeposited substances on the surface.

The brass usually specified for adhesion contains 70 per cent copper and 30 per cent zinc, but this is an oversimplification, since rubbers have been bonded perfectly to brasses ranging from 60 to 80 per cent copper. Rubber
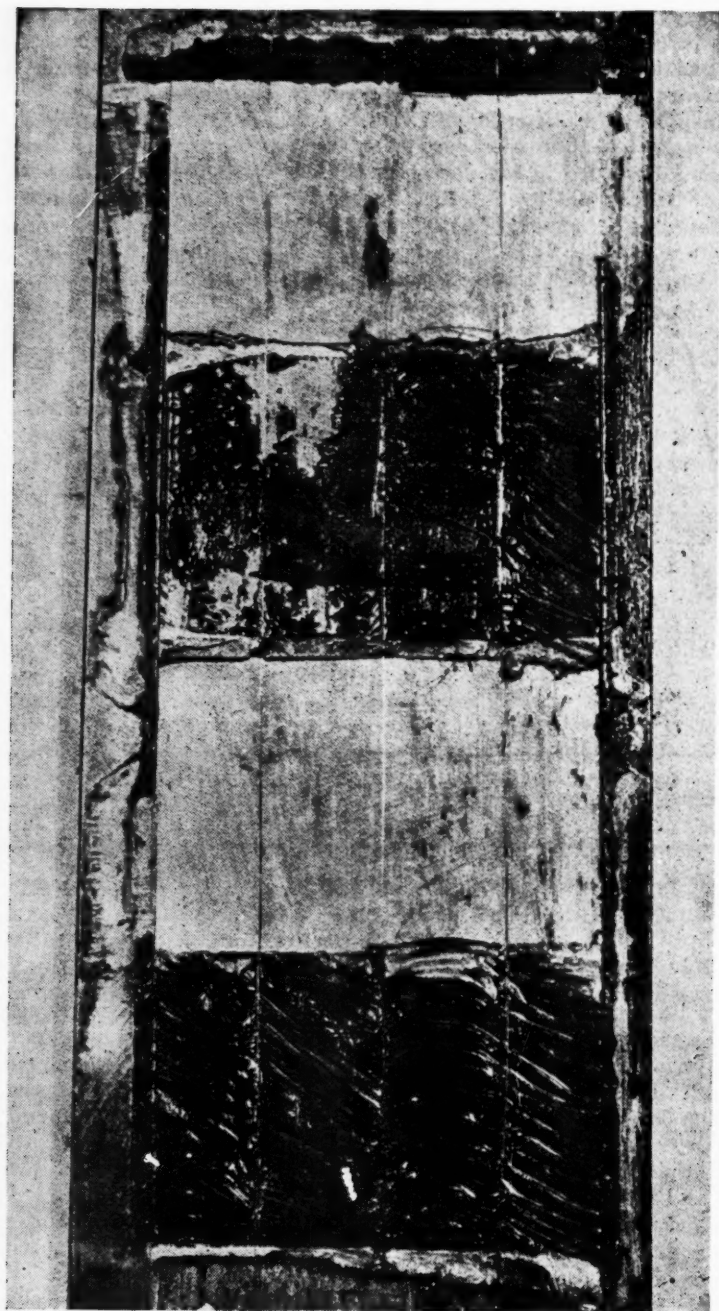
FIG. 2.—Effect of accelerator content on bond.

MBT (per cent.)

will not generally adhere to a brass that is pinkish, that is, above 85 per cent, or below 58 per cent Cu.   The pink coloration below 58 per cent appears to be due to the formation of beta or gamma brass, and the transition from good to zero bond is sharp.   At about this composition there is a similar change in the mechanical properties of brass.

Experiments show that the type of brass for best bond varies with the compound employed.   Figure 3 shows the change in bond produced by increasing the copper content of the brass by raising the temperature of the plating bath, for the various compounds given in Table 2.
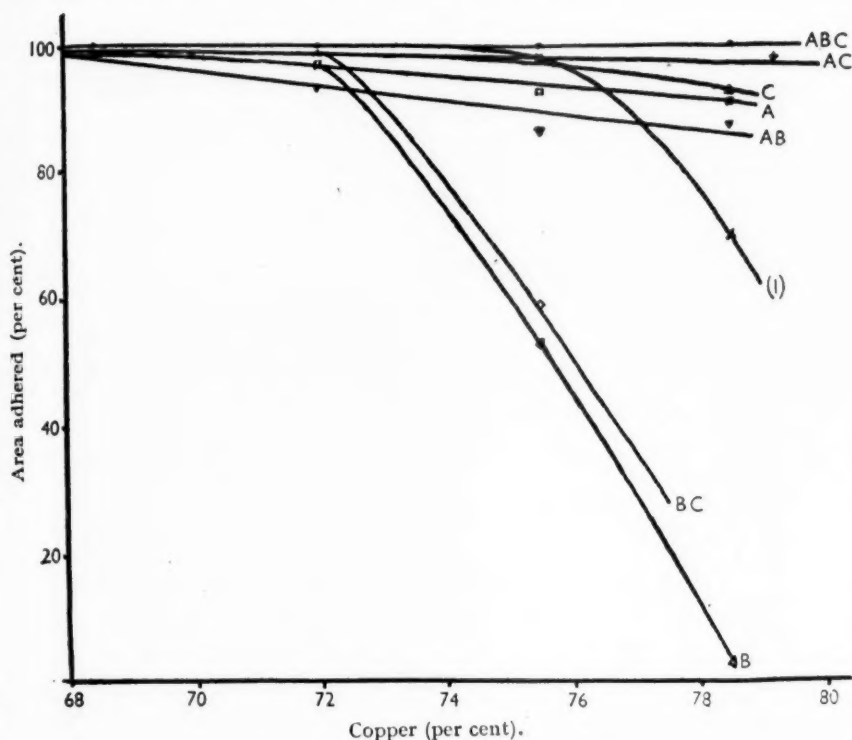
FIG. 3.—Effect of Brass Composition on Bond.

TABLE 2

Base Mixing:—Rubber, 100; stearic acid, 3; gas black, 60

	(1)	A	B	C	AB	AC	BC	ABC
MBT	0.25	1	0.25	0.25	1	1	0.25	1
S	3	3	3	8	3	8	8	8
ZnO	5	5	30	5	30	5	30	30

All these compounds were cured for 40 minutes at 307° F.

The diagram shows a general tendency for adhesion to fall as the copper rises, but the rate at which it falls off depends markedly on the compound. Compounds with 1.0 per cent MBT (marked A), and those with 8 per cent

sulfur (C, AC, BC, ABC) maintain their bond well, but the opposite cases with the low accelerator and low sulfur fall off rapidly as the copper rises above 73 per cent. Inspection of the curves shows further that high zinc oxide (B) accentuates this effect.

As this experiment was already complex, the effect of various cures was not studied, but the results might have been different if each compound had been given its optimum cure.

A striking demonstration of the dependence of bond on the agreement between compound and brass is shown in the photograph of Figure 4. In this
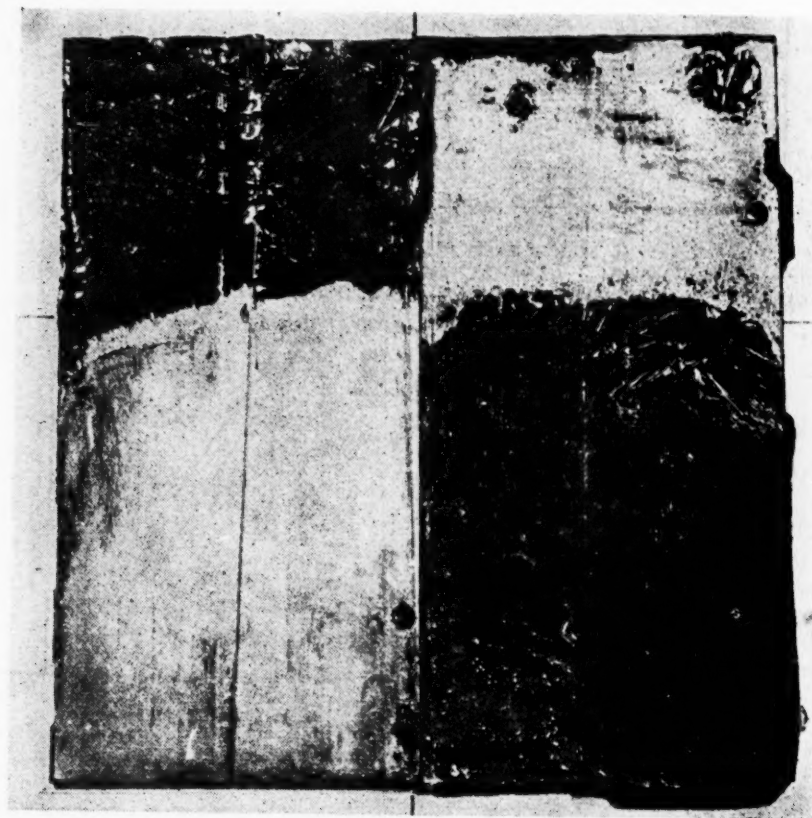
Bath D 67% Cu.

FIG. 4

Bath C 82% Cu.

case two steel-plates were plated in different baths and moulded side by side with two compounds laid across them. The upper compound, a 50-rubber 50-GR-S mixing, adhered to the 67 per cent copper brass, but not to the high-copper brass. With the lower one, on all rubber compound, the reverse was the case. Whether the difference in bond was due to the crude material used, or to other factors in the compounds is not certain, but this does not affect the conclusion that the compound and brass must be suited to one another if an effective bond is to result.

As regards the second possibility, that the crystal structure of the brass affects its activity, the work of Gwathmey and Benton[8] has shown that the chemical activity of copper, at least, depends markedly on crystalline orientation.   There are grounds for believing that difficulties due to this cause occur when a new bath is being started, but with established baths in regular work, variations that do occur are usually associated with change in composition of the deposit and can be overcome by correcting the composition.

Both crystal structure and adsorption are difficult to study, and methods of controlling them are not known.

Third factor: Moulding conditions.—The points in moulding that are relevant are pressure, rubber movement, amount of heating, and rate of heating.   As regards pressure, and rubber movement, although in practice they may be of considerable importance, the effect is largely a mechanical one of placing the rubber in the right place at the right time[6].   From the chemical standpoint the amount and rate of heating are of more interest.   Buchan[4] has said that the bond is independent of cure, and the author[6] was formerly of this view, but later work has shown that this opinion must be revised.

TABLE 3

Cure (min.)	7	10	20	60
Adhesion	none	fair	good	none

Table 3 shows the effect of cure at a steam pressure of 60 lbs. per sq. inch of a natural rubber mixing accelerated with mercaptobenzothiazole and tetramethylthiuram disulfide.   The metals used were all plated at the same time, and similar results were obtained with platings from two different baths.

TABLE 4

MBT content	Cure (min.) at 307° F			
%	12	20	40	60
$\frac{1}{4}-\frac{1}{2}$	perfect	poor	none	none
$\frac{1}{2}-\frac{3}{4}$	perfect	fair	very poor	none
$\frac{1}{2}-\frac{3}{4}$	perfect	good	very poor	very poor
$\frac{3}{4}-1$	perfect	good	very poor	very poor

The results in Table 4 obtained with a 50-rubber 50-GR-S mixing containing lampblack and varying amounts of mercaptobenzothiazole.

In this case the effect produced is a function not only of the length of cure, but of the amount of accelerator.   These results have been confirmed by later work.

A comparison of the two tables indicates that low accelerated stocks are good at short cures but fail at overcure, whereas prolonged cures are necessary to develop a bond with highly accelerated rubbers.   Thus, the best acceleration depends on the moulding technique.

The earlier results, in which bond was independent of cure, were probably obtained with flat-curing rubbers with moderate acceleration.   The effect of cure is only pronounced in marginal conditions.

The effect of rate of heating has not been studied so fully, but preliminary results suggest that slow heating favors the attack of the brass by sulfur[6].

Effect of rubber on copper.—A study of the effect of variables in brass-plate bonding would be much facilitated if one of the factors could be kept constant.   This may be done, if it be assumed that the reactions are the same,

by replacing the brass by solid copper sheet. When rubber is moulded into this, a sulfide layer is formed, which usually adheres to the rubber. By estimating the copper adsorbed in this way on unit area of the compound, the activity of the rubber in attacking copper may be measured.

Table 5 shows the amount of copper absorbed by rubbers of the usual

TABLE 5

MBT	0.25	1.0	2.0	0.16	0.65	1.3
TMT	—	—	—	0.05	0.20	0.4
Copper adsorbed (mg. per sq. cm.)	8.24	4.47	1.35	7.15	3.88	1.15

formula with six kinds of acceleration.

As acceleration increases the attack on copper rapidly falls. This is in exact agreement with the findings with brass-plating. Later experiments suggest that the attack on copper is inversely proportional to the accelerator content.

As an increase in vulcanization rate results in a reduced sulfide formation on copper, there is a strong suggestion that the rubber and copper are competitors for the sulfur. Support for this is given by Dason[9], who found that sheets of rubber cured between copper plates were appreciably less cured than others moulded between steel plates, due to the removal of sulfur by the copper.

Table 6 shows that high acceleration apparently puts an upper limit to the sulfide formation, even when the sulfur is increased.

TABLE 6

COPPER ABSORBED BY RUBBER COMPOUND (MG. PER SQ. CM.)
Sulfur in compound

MBT	$\frac{1}{2}$	1	2	4	6
$\frac{1}{4}$	—	—	5	7.6	9.8
2	0.7	0.9	0.9	0.6	1.15

Even with low accelerator, the increase in sulfide is much less than the increase in sulfur, a conclusion which is in accord with the small effect of sulfur changes on brass-plate bonding.

The copper absorption method shows close parallels to the brass plating process. Similar results for the effect of copper on rubber have been given by Satake[10].

Mechanism of bonding.—The experiments with copper sheet show that a visible layer of copper-bearing material is formed at the junction of copper and rubber by the action of the sulfur in the mixing. It is reasonable to suppose that this interlayer, if not the actual adhesive, is at least intimately connected with the adhesion.

The amount of copper-sulfur-rubber reaction product formed on solid copper sheet is many times greater than can be formed on brass. The amount of copper taken up by usual compounds is about 4 mg. per sq. cm., but the total amount of brass usually deposited is only of the order of 2 mg. per sq. cm. The reaction with brass must, therefore, be much slower than with copper.

In all adhesives a certain minimum is required to give a bond, but an excess of bonding agent again gives a weak joint. This has been demonstrated by McBain and Hopkins[7] for glue and shellac, and by Crowe[11] for solders. It may, therefore, be expected that the brass-plate bond will fail if the amount of adhesive reaction product is too small or too large. The reaction is increased by

the amount of cure and by increased activity of the brass, and opposed by the vulcanization of the rubber. A satisfactory bond results only when these factors are balanced. From this point of view the 70/30 brass usually specified for bonding is that which has the correct activity for rubber stocks which are satisfactory in general properties, and which can be handled by ordinary procedure. Zinc is here regarded merely as a diluent, but the role of zinc salts in compounding makes it possible that it is especially suited for this purpose.

The theory that the brass-plate bond depends on the formation of an adhesive, and that this is opposed by the vulcanization of the compound, not only explains the practical requirements for efficient bonding, but accounts for the complexities of the problem. For consistent bonding to be maintained, at least four variables have to be under control, and suited to one another, *viz.*, the vulcanization properties of the rubber, the nature of the brass, the total cure, and the moulding conditions. It is not surprising that the process has a reputation for being erratic, if these are not properly controlled.

The general conclusions of this paper are not affected by the exact nature of the reaction product, whether it involves oxidation, cyclization, or so on, but it is likely that further study of the problem would give valuable information of the action of accelerators and the nature of vulcanization.

ACKNOWLEDGMENT

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PHYSICAL EXAMINATION OF BRASS DEPOSITS *

S. Buchan and W. D. Rae

The process of bonding rubber to metal is of very great importance to two major industries, rubber and engineering.   The method which has received the most attention in this country, and which is undoubtedly the most satisfactory when properly controlled, consists of bonding rubber to metal by means of an intermediate layer of electrodeposited brass.   This method was developed on a production basis in America between 1920 and 1930, but since then little comprehensive research has been carried out, and what has been done has dealt mainly with the production of suitable bonding rubbers or with the more straightforward reactions which occur in the depositing bath.   For years the method was worked as a secret process, and little information has, therefore, been published.   Even sixty-five years after its inception (it was known in 1879) the theoretical principles involved have not been explained, and the consequence is a lack of understanding and standardization in the methods and conditions employed.

It is natural to assume that research would first of all develop towards the attainment of good bonding rubber stocks and accurate scientific control of the brass plating solutions. (This has, in fact, been the case, and the majority of published papers deal with these two aspects of the problem.) For example, Ferguson and Sturdevant[1] investigated the significant factors in the plating solution which affect the chemical composition of the brass deposit, and outlined the best conditions for obtaining a brass deposit of composition 70 per cent copper and 30 per cent zinc.   Similar papers were also published by Coats[2] but with special reference to adhesion of the plating to rubber.   Since then a few papers have appeared dealing more particularly with various aspects of the plating solutions, such as ammonia content, free cyanide and other specific factors.

McCortney[3], appears to have initiated research on the rubber side.   The action of the various compounding ingredients, in particular the choice of accelerators, was studied by him.   Coats[2] also dealt with the question of rubber stocks.   These investigations were of a qualitative nature, and no attempt was made to reason out why adhesion was improved by the presence or absence of certain materials.   One of the authors[4] established that sulfur was necessary for bonding.   This was substantiated by Gurney[5].   It, therefore, seemed to be a hopeful line of research on the chemical nature of the bond.   Further experiments revealed that adhesion could be obtained to brass deposits of different composition, e.g., 70 per cent copper, 75 per cent copper, 80 per cent copper, by making changes in the rubber stock.   Evidence seemed to indicate that the answer to this lay in the relative velocities of the reactions of rubber with sulfur and sulfur with brass, good adhesion being obtained when a proper balance is struck between these two velocities.

It was apparent from time to time that adhesion was not obtained to brass of 70 per cent copper–30 per cent zinc composition, although all known conditions necessary for obtaining adhesion had apparently been satisfied, and it seemed clear that a full investigation of the physical nature of the brass was required in addition to a study of its chemical composition.

The physical aspect with which this paper deals consisted essentially of comparison under the microscope, electron microscope, and x-rays of brass which bonded satisfactorily to rubber and brass which did not.

In an investigation of this type one of the main difficulties has been to produce plating which gives good or bad bonding brass at will. It has been noticed, however, that when a plating bath is newly prepared, bad bonding brass is produced for some time, although the percentage composition of the brass may be correct, but that continued electrolysis of the solution rectifies this condition. It was decided to make use of this known condition for the preparation of deposits of good and bad brass for examination.

The plating solution was made up and the percentage of copper in the deposit adjusted to 70 by means of continued electrolysis and additions of approximate amounts of ammonia. As soon as this condition was achieved a 4 × 2 inch hardened steel plate which had been highly polished and lapped was plated alongside a standard adhesion test plate. Electrolysis was continued, and similar pairs of test plates were taken from the bath every three hours until adhesion was obtained. Final test-plates were taken from the bath one week after the attainment of adhesion.

A standard method of testing the bonding properties of the brass was adopted. A mild steel plate 4 × 2 × 1/16 inch was plated and bonded in a mould, under constant hydraulic pressure, to a standard good bonding rubber stock. Vulcanization was carried out under standard conditions of time and temperature. After vulcanizing and cooling, the test-plate was taken, and a cut made through the rubber down to the metal at one end. The rubber was then pulled off slowly by hand with pincers. If any brass was exposed by this means, the bond was regarded as being substandard. If this was not the case and the rubber tore, usually in the vicinity of the metal surface but showing no bare brass, then the bond was classed as being good. This test was regarded as more selective than a straightforward pull, either in tension or in shear, carried out usually on a sandwich-type of test unit.

Various factors can influence the physical nature of the brass deposit, and it is well to examine some of these before detailing the results obtained by physical examination. A more complete picture can thus be obtained. In electroplating, the plated layer tends initially to assume the structure of the base metal. If the cleaning treatment of the base metal is cathodic, excessive gassing may distort the metal surface somewhat and, consequently, unless this absorbed gas is removed later in the process, e.g. by anodic treatment, attempts to deposit brass on that surface may yield distorted brass plating. Such distortion can also be caused by excessive gassing while the surface is being plated, the amount of gassing in this latter case being determined by the nature of the metal surface which largely controls the hydrogen over-voltage. It would, moreover, appear that the pH of the solution and also its ammonia content have an influence on the effect of gassing at the cathode. From experience of plating for adhesion purposes, some gassing is beneficial, and dull opaque plating (very small crystals caused by gassing) is more satisfactory than bright shiny plating, which consists of somewhat larger crystals produced under cir-

cumstances which did not allow of much gassing. Too much gassing, however, may lead to a porous deposition which is equally objectionable, and care must be taken to see that the evolution of gas is kept within reasonable limits.

EXPERIMENTAL RESULTS

The surface contours and crystalline structure of an average plate surface was studied under the microscope, and those of a highly polished surface by the electron microscope. x-Rays were used to determine the relative states of strain, the lattice spacing, and crystalline orientation of the brass layer. From this examination it was hoped to discover some physical factors which might influence the bond obtained between rubber and brass.

Microscope examination.—No clearly defined crystalline form could be identified. The crystals which were extremely small were collected in numerous aggregates or hillocks over the surface of the plate. These hillocks were larger and more plentiful along grooves in the metal when such relatively deep grooves did exist (Figure 1).
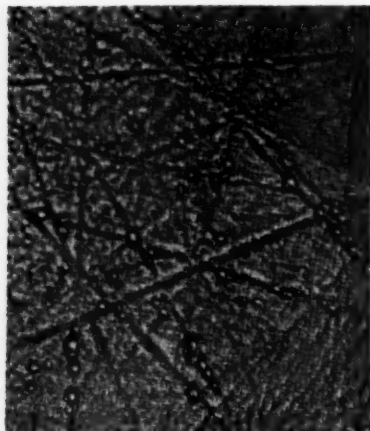
FIG. 1.—Micrograph of good-bonding brass.
Magnification ($\times$ 2000).

FIG. 2.—Brass-plated steel strip.
Magnification ($\times$ 10).

The appearance indicates grinding marks under the deposit. Some strained areas are also shown.

The first test-plate examined consisted of a steel strip $4 \times 1\frac{3}{4} \times 1/10$ inch. This was brass-plated in a bath which gave at the time good bonding brass. Under magnification ($\times$10) some strained areas were revealed on the surface of the deposit, but the state of strain over the surface of the metal was definitely not uniform (Figure 2). Cross-section examination (Figure 3) showed that the brass deposit had an average thickness at the edge away from the hole of 0.0006 inch and at other points on the plate away from the edges 0.00004 inch. At the centre of the plate, however, the brass deposit was extremely thin. The layers of brass near the edges of the plate were not uniform throughout, those nearest the steel being copper-colored, those next to that, a mixture of α- and β-brass and on top α-brass. Away from the edges the deposit was more uniform throughout its depth, no β-brass being identified. Further it was

noted that β-brass occurred where cavities existed between the brass and the steel. Those cavities appeared to be caused by similar cavities in the steel itself (Figure 4).

Etching of the surface with hydrogen peroxide and ammonia (9 parts H_2O_2 to 1 part 0.88 ammonia) revealed a cellular structure in all cases (Figures 4 and 5). Whether this was the real structure of the brass or mere pitting of the metal could not be determined.

FIG. 3.—Brass-plated steel clip.
Magnification (× 2000).

Cross-section of the test-strip extending towards the centre (bottom), showing the variation in thickness of the deposit over the surface of the plate.
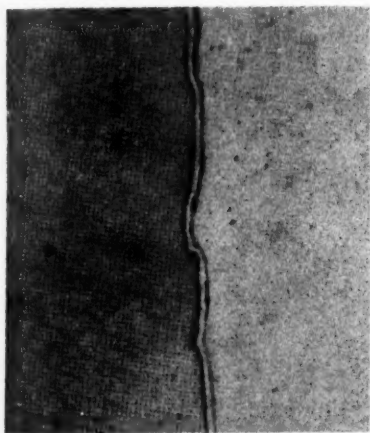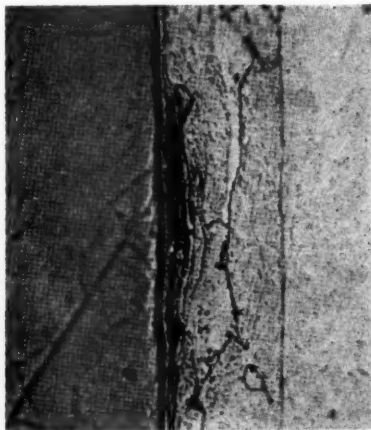
FIG. 4.—Etched plating.
Magnification (× 1500).

Cross-section of test-strip taken from near the bottom edge. Steel is on the left of the deposit and a brass clip is on the right. An irregular copper-colored deposit appears adjacent to the steel. Note the cavities which occur below the copper-colored deposit.

The next step taken was to compare good-bonding and bad-bonding samples of brass to see if any real physical difference existed between the two. Brass deposits of the same chemical composition were used, but microscopic examination failed to reveal any appreciable difference between the two, almost identical photographs being obtained in both cases.

The electron microscope.—Microscopic examination having failed to give any clue to the crystal structure, it was decided to go to higher magnifications, and for this purpose the electronmicroscope was used. Photographs were taken at magnification of 3000.

For the satisfactory examination of electrodeposited brass by this means, it is essential that the surface be smooth. Preliminary experiments had, therefore, to be made to find what degree of polishing of the base metal was required, and, having obtained a smooth base, to discover if the plating deposited on it was sufficiently uniform. A highly polished surface is necessary because of the technique involved. A resin cast of the surface is prepared, and it is this resin cast which is mounted in the electron microscope and examined. It is prepared as follows. A pool of liquid gelatin is allowed to set and then to dry on the surface under examination. When the film dries it is easily detached from the surface. The side carrying the impression of the brass is then coated with a thin film of the resin, polyvinyl-formal, which is then

freed from the gelatin by dissolving the latter in water. Since under examination in the electron microscope, electrons are passed through the resin film to obtain the photograph, the film must neither be too thick (not greater than 1/25 of a thousandth of an inch), nor must the surface be too irregular. If the deposit is too rough, the film will of necessity be thin at points of depression on the surface, and invariably breaks, so it is impossible to obtain a satisfactory electron micrograph.

It was found that hardened steel which had been polished and lapped gave the best results. These plates were polished to as smooth a surface as possible with emery cloth. They were then lapped, using a suspension of fine carborundum powder in a turpentine base. Paraffin which is usually employed in such lapping operations was not used because of difficulty experienced in
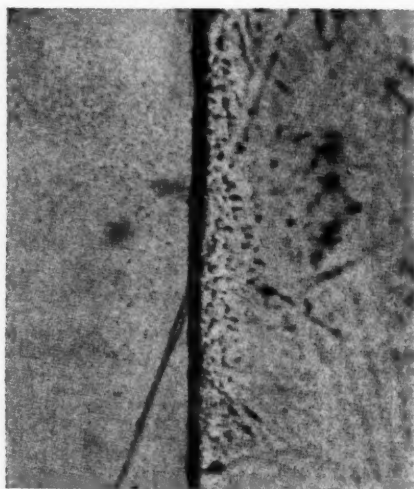
Fig. 5.—Etched plating.   Magnification ($\times$ 2000).
This is a similar cross-section of the plate to that shown in Figures 3 and 4.
The cellular structure produced by etching is shown.

removing it completely before plating. Figure 6 is an electron micrograph of a deposit obtained from a bath which had been giving good bonding brass for several weeks, and shows that the surface comprises a number of closely packed "hillocks", many of which have a polygonal outline.

Other plates were prepared in the same way and plated at intervals from the time the bath was made up until adhesion was obtained (a period of about 1 week). The composition of the deposited brass was first of all brought to the correct value merely by continued electrolysis before the first plate was taken out. Adhesion, which was tested as above, was nil. Three hours later a second plate was taken from the bath. Adhesion was again nil. Thereafter electrolysis was continued for about a week until adhesion was obtained, and as soon as this was achieved a third plate was taken. One day later a fourth plate was taken from the bath. The results were as follows, and are illustrated in the electron micrographs (magnification $\times$3100), shown in Figures 7, 8, 9, 10.

It is evident from these results that a definite change takes place in the nature of the deposited brass in passing from bad adhesion to good, but no

clue could be obtained from the electron micrographs as to the factors which bring this about.

x-Ray analysis.—Two methods of x-ray analysis were adopted (1) glancing incidence, and (2) back reflection.

Photographs taken by glancing incidence showed that, in every case, the deposit was wholly α-brass. No lines corresponding to β-brass were observed. In the first test-plate examined, which was mild steel, no marked preferred orientation was found. Strong lines of α-iron and faint lines of cementite also were visible.
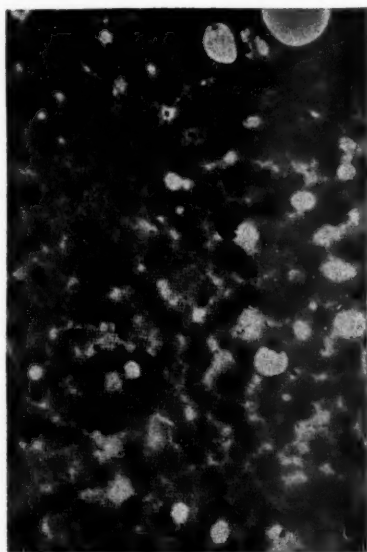
Fig. 6.—Electronmicrograph of a sample of standard good-bonding brass plating. Magnification ($\times$ 3100).

Examination by the back-reflection method of the same specimens that were used in the electronmicroscope revealed large differences in the lattice spacing exhibited by good-bonding brass and by bad. Two factors were known to have an effect on the lattice spacing, (1) distortion of the lattice due to strain, (2) the chemical composition of the deposit. Photographs were taken of pure copper and of cast brass, 70 parts copper and 30 parts zinc (Figure 11). By measuring, on the x-ray negative, the spacing for the copper in both these samples, a difference of 3.5 mm. was obtained. This, therefore, corresponded to a difference in composition equivalent to 30 per cent of copper, or 8.57 per cent of copper per mm.

A difference of about 1 mm. in the space-lattice dimensions was found between the good and the bad brass. This, if it were solely due to the difference in chemical composition, would mean a difference of nearly 8.6 per cent copper, which was not borne out by chemical analysis, the difference being only 2 per cent. On the other hand the large difference could not be solely accounted for by assuming a state of strain in the brass, as the strain imposed
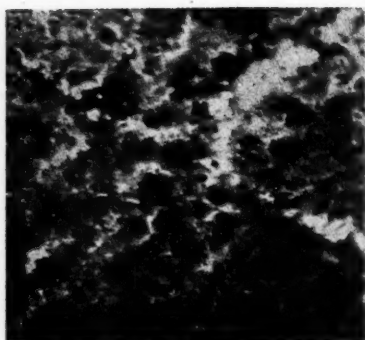
FIG. 7.—A sample of brass plated in a freshly made brass-plating solution. Adhesion to rubber was nil.
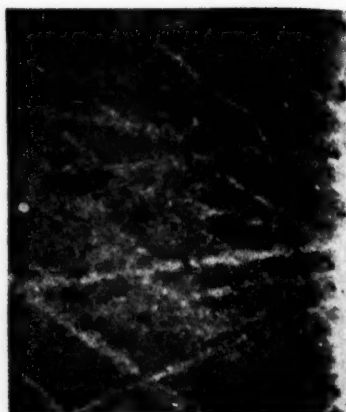
FIG. 8.—A sample plated in the same bath three hours later. Adhesion was again nil.
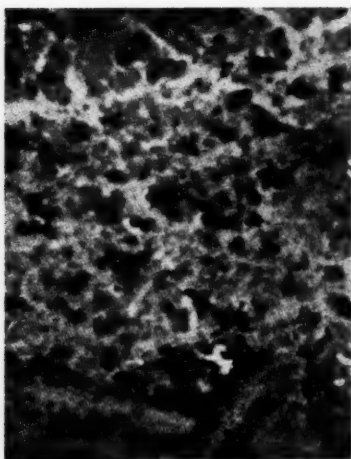
FIG. 9. A sample plated in the same bath as soon as good bonding brass was obtained.
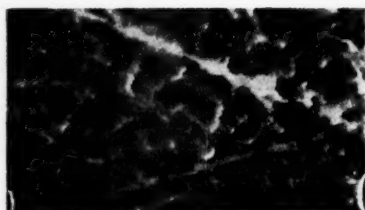
FIG. 10.—A sample plated in the same bath one week later. Adhesion to rubber was good. Note the resemblance to Figure 6.

	Plate	Percentage copper	Adhesion	Remarks
1.	(Fig. 7)	66.1	Nil	A very fine grained surface with large streaks was obtained. It was entirely different from previous micrographs.
2.	(Fig. 8)	68.6	Nil	Still fine grained, less streaky, more uniform.
3.	(Fig. 9)	69.4	Good	Surface still more uniform, somewhat larger grain.
4.	(Fig. 10)	68.4	Good	By this time the photographs began to resemble the first micrographs obtained, *i.e.*, those of a plate from a bath which had been electrolyzed for several weeks.
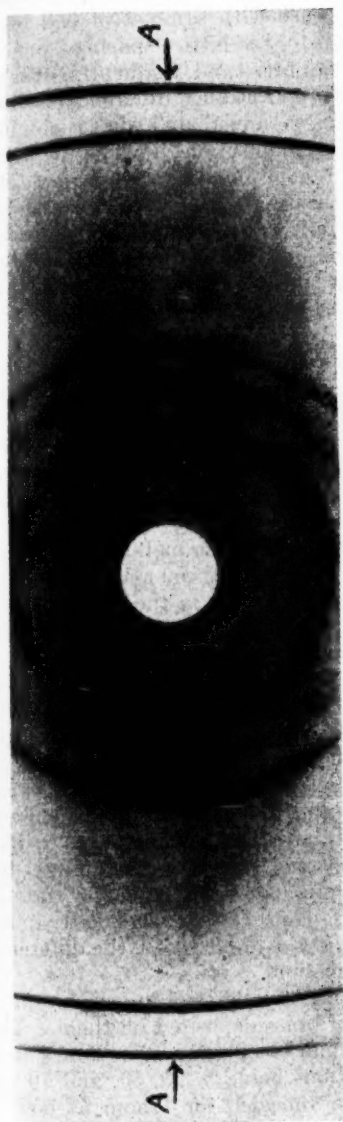
FIG. 11.—Back reflection x-ray Photograph of Normal 70—30 cast Brass.
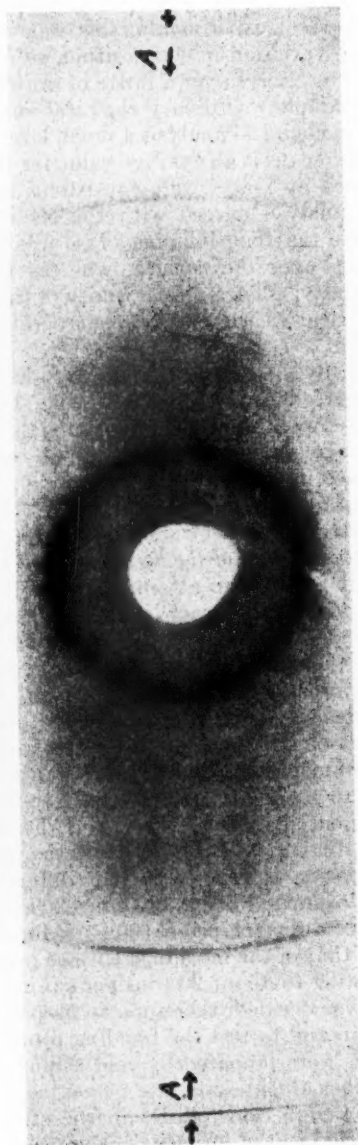
FIG. 12.—Back Reflection x-ray Photograph of Electrodeposited Brass. The dark complete ring in the centre is due to the base metal, iron.

would be greater than the tensile strength of the brass. The maximum strain would account for about 0.5 mm. spacing. It was noticeable, however, that whereas the lattice spacing in the case of good brass was found to be consistent over several experiments, this was not the case with samples of bad brass. A wide variation in composition, as measured by the lattice spacings, was obtained by x-rays over a range of samples of bad brass and, frequently, over the same sample. Ordinary chemical analysis showed no such differences. However, in chemical analysis a much larger area is examined, and what is obtained by this means is an average value for the brass composition. Where the values obtained by x-rays were consistent, e.g., on a good-bonding brass sample, the x-ray analysis agreed with the chemical analysis. These results seemed to indicate that bad-bonding brass was characterized by nonuniformity of composition over the surface, whereas good-bonding brass showed pronounced uniformity. The nonuniformity of the surface of samples of bad brass was also made clear in the electron micrographs to which reference has already been made.

Finally, other points were considered, such as differences in crystallite size and degree of crystalline orientation, but there appeared to be consistent differences between good and bad samples in these respects. All specimens showed a high degree of preferred crystalline orientation. This is shown by the disappearance in electrodeposited brass of the inner complete rings shown in the photographs of normal cast brass (Figure 12). This type of orientation is characteristic of electrodeposits.

*The influence of the base metal.*—The state of the base metal plays an important role in the attainment of adhesion. This has been most noticeable when dealing with cast iron. Identical metal parts cast in the same foundry and under the same conditions gave totally different results when bonded. Since, therefore, these casting were to all intents and purposes identical, it would appear that the machining process to which the bonding surfaces were subjected must have had a decided bearing on the ease of plating and on the amount of adhesion ultimately obtained. It was found that the higher the speed of machining and the more concentrated the cutting oil, the more difficult it was to get a satisfactory brass deposit. Microscopic analysis did not reveal any essential difference between the higher and lower speeds of machining, except that a smoother surface was obtained with the higher speed. x-Ray examination showed a further difference between the two machinings, the speeds examined being 1000 and 200 ft. per min., respectively. The state of strain of the machined surface produced at the higher speed was greatly in excess of that of the machined surface produced at the lower speed, the difference amounting to about 20 tons per sq. in. compression.

It was decided, therefore, to prepare samples of mild steel in various states of strain and to test the bonding properties of brass deposited on them. The samples were prepared by cold rolling eight mild steel strips 12 × 2 × ¼ inch to various thicknesses, the percentage reductions being 5, 25, 50, and 70 per cent. Before cold-rolling, all the strips were annealed for 1 hour at 650° C and cooled in the furnace. When cold, the strips were pickled in 15 per cent sulfuric acid, containing 0.05 per cent of an inhibitor, maintained at a temperature just below boiling point. The strips were vigorously scrubbed with a wire brush, and when all scale had been removed, were washed with water to which a little ammonia had been added, and then with methylated spirits. The strips were allowed to dry and were cold-rolled, two samples being prepared for each

state of strain. One of each of these was annealed for 1 hour at 650° C, and furnace-cooled.

All samples plated with equal ease, and no visual difference was noticeable in the appearance of the brass deposit. Also, chemical analyses showed them to have the same composition. Good bonds to rubber were obtained with all the samples, and from this it can be deduced that strain, provided it is distributed evenly over the surface of the metal, is not detrimental to the adhesion of rubber stocks to brass.

Conclusions.—Whereas the lattice-spacing of the brass is important from the point of view of bond formation, two other factors are of equal importance, and are interconnected. They are the amount of oil present in the pores of the metal and the uniformity of the surface produced. Absorption of oil by the metal appears to cause distortion and results in a nonuniform surface. This nonuniformity is a contributory factor in cases of failure to obtain a good bond. Lattice-spacing, although affected by distortion of the base metal surface, is on the whole determined by the composition of the deposited brass. Where the lattice-spacing is uniform over the whole plated surface, adhesion of rubber can be obtained to plating of any composition between 70 per cent copper and 80 per cent copper by adjusting the rubber quality to suit the particular brass composition.

SUMMARY

Microscopic examination of average brass deposits revealed a fairly uniform deposit of thickness varying from 0.0006 to 0.00004 inch, the brass deposit being thinner at the centre of the plate than at the edges.

β-brass was obtained at points where porosity occurred in the base metal. The deposit was collected in aggregates or hillocks dispersed fairly evenly over the plate, a condition which was confirmed by examination under the electron microscope. With this instrument it was demonstrated that bad bonding brass was nonuniform over the surface, a fact further substantiated by subsequent x-ray analysis. Differences in crystallite size and in degree of crystalline orientation appeared to have no consistent effect on the bonding properties of the brass. The brass deposit showed, however, a high degree of preferred orientation, as is usual with electrodeposits.

As regards the preparation of the base metal, the use of too much oil and too high a speed of machining appeared to have a detrimental effect. This appeared to be due to the fact that a nonuniform state of strain was produced over the surface as samples of mild steel of various degrees of strain, but uniform over the surface, gave consistently good adhesion.

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COOLING FACILITIES OF RUBBER EQUIPMENT *

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Proper maintenance of rubber processing equipment is a necessary and important phase of production. If management is to maintain maximum overall production it must allow the engineering and maintenance organization sufficient authority, time and money to keep equipment operating at top efficiency. When the pressure of production jobs that have to be completed "yesterday" interferes repeatedly with repairs that should have been made last week, the chances are very good that a condition will soon exist where the rush job can not be completed until next month. The first rule, then, in maintenance work is, *"Do it now."* A small repair job today may prevent a costly shutdown tomorrow.

In addition to the mechanical difficulties regularly occurring, there are a number of little things that frequently cause production delays and hidden extra costs. One of the most important of these concerns the cooling of mills, Banbury mixers, calender rolls and tubing machines.

Early in the history of the rubber industry it was learned that some means of carrying off heat occasioned by friction of the stock working on the equipment was necessary. It was learned later that the same facilities could be used to control temperatures within the ranges suited best for a given stock or processing operation. The methods in use today have altered little since the first installations were made, but it is doubtful that full use is always made of the facilities available. In ordinary times this was foolish and expensive. Today it approaches sabotage by interfering with production, increasing the percentage of seconds, and wasting vital raw materials.

Most causes of inadequately cooled processing equipment are obvious, and their correction is generally inexpensive and elementary. However, as is often the case, the obvious little things are all too frequently overlooked and unsatisfactory conditions tolerated. It is hoped that, by pointing out potential trouble spots and emphasizing both the processing difficulties due to poor cooling and the ease with which they may be corrected, much future trouble may be avoided.

MIXING MILLS

First, let us look at the rubber mixing mills, one of the first items of processing equipment used in the industry. Fundamentally, there is little difference between the oldest 40-inch mill and the most modern 84-inch mill except for refinements. One of these involves the use of steel rolls, because their greater strength makes possible the use of a thinner shell having faster heat dissipating qualities.

Improper cooling of mill rolls may contribute to the following production problems:

1. Stock too hot to handle conveniently—a potential safety hazard.

2. Poor quality of vulcanized stock, due to prolonged exposure to high mixing temperatures.

3. Partially scorched stock.

4. Loss of softener, due to vaporization at mixing temperatures.

5. Sticking of stock to mill rolls.

6. Extended mixing cycles, due to the reasons above and to waiting for mill to cool before starting succeeding batch.

If you have these or other problems that may be due to improper cooling, check the following points:

(1) *Water Supply to Mill.*—Is the flow of water to the mill the full capacity of the pipe or are the pipes corroded or full of scale so there is only a trickle of water?

Solution.—Replace piping from main supply to mill, using pipes of adequate size.

(2) *Valves.*—Are all valves in good working order and open? Faulty valves which do not open fully—or even a good valve if it is kept closed—prevent cooling water from doing its job. In open-end mills this can be easily checked. In closed systems, it is more difficult to make sure that the flow of water is unimpeded, since it is also necessary to make sure that a valve or fitting in the outlet line does not build up back pressure and restrict the flow of coolant.

Solution.—Make sure that all valves—both inlet and outlet—are in good working order. Repair or replace faulty valves and keep them open when using the mill.

(3) *Spray Pipes or Water Distributor Pipes.*—Have spray pipes been checked to be sure they are functioning properly? One good indication of faulty spray pipes is a mill roll surface cool at the inlet end, but progressively hotter as you approach the opposite end.

Solution.—Remove spray pipe and either repair or replace it. The spray pipe should be closed off at the end opposite the inlet and should have small holes drilled along its length. It should be installed so that the water will be sprayed against the inner top surface of the rolls to give maximum cooling efficiency.

(4) *General Overheating.*—Does a mill heat up rapidly, get too hot during use, or cool down slowly? If the answer is "yes" or if it is impossible to operate 24 hours a day without either running into difficulty or giving the mill a cooling-off period, the mill is probably not making full use of the cooling water. Over a period of time deposits of rust and calcium salts from the water build up on the inside of the mill. The foreman in your boiler room or power plant can give you an excellent story of the effectiveness of hard water scale as a heat insulator and the need for keeping the boiler tubes clean. Cooling a mill is the same story in reverse. A deposit of only a fraction of an inch cuts the effectiveness of cooling water in half; and the heavy deposits common in many plants make it impossible for any amount of cooling water circulated to be effective.

Solution.—Clean out the mill rolls by means of iron jacks or chemicals.

(a) *Jacks.*—Get a supply of about $1\frac{1}{2}$-inch iron jacks from a local foundry. Ten or fifteen pounds of jacks suffice for an 84-inch mill, with proportionately smaller amounts for smaller mill rolls. After disconnecting the water-supply pipes, load the jacks into the mill through the water inlet. They may be easily pushed through the mill-roll neck with a stick. Now reconnect the water piping and run the mill with a full flow of water for several hours. In

closed systems, it is advisable to have the mill end open during the first few hours to prevent the dirt and scale knocked loose from clogging the outlet pipes and drain. Any jacks remaining in the mill after it is clean cause no harm, but help prevent scale from building up again as the mill is used.

(b) *Chemicals.*—The water-cooling system is turned off and mill rolls are drained by siphoning. Then a prepared scale remover, such as Duclean No. 2*, diluted according to directions, is poured into the rolls. The rolls are then allowed to turn for 30 minutes to 1 hour. The water is turned on again, and the chemical solution and removed scale flushed to the drain; the mill is then ready for use.

Another simple and practical method for removing scale with chemicals is illustrated in Figure 1. The chemical cleaner is made up in the drum to the
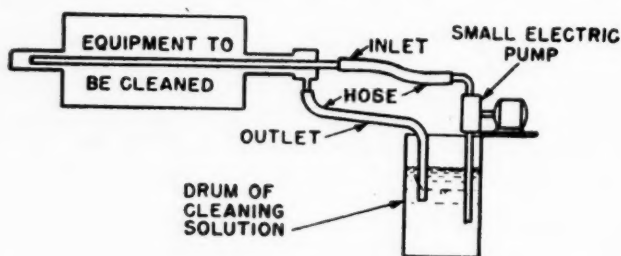
FIG. 1.—A typical set-up for cleaning scale chemically from the internal surfaces of mill rolls, Banbury rotors, and jackets and screws of tubing machines.

desired concentration, making allowances for dilution by the water in the equipment to be cleaned. The cleaner is circulated by the pump while the equipment is operated.

The comments on mixing mills apply generally, but with specific variations, to the other principal pieces of processing equipment in the rubber shop.

BANBURY MIXERS

All of the later Banbury Mixers are equipped with spray type cooling of the shells, and it is a simple matter to lift the curtain and check the spray nozzles. But it is amazing how often even this precaution is neglected. A regular daily check is advised. A few choked nozzles and cooling efficiency suffers materially. Hence, don't just look. When a spray nozzle is not working properly, take a few minutes to have it cleaned out—or better yet, have spares on hand for prompt replacement. And make the replacement now. The baffles and plates should also be checked regularly and a definite schedule set up for cleaning and scraping away deposits of rust and scale.

Follow the schedule religiously. Scale on the outside of the shell or the inside of the rotors of a Banbury Mixer can reduce cooling efficiency just as it does on the inside of a mill roll. While it is impractical to use jacks in Banbury rotors, scale and calcium deposits may be removed by the use of Duclean No. 2, using the set-up shown in Figure 1. Be sure to keep the rotors turning while they are being cleaned.

Rotors, ram and slide have flexible hose inlets, and generally discharge into an open drain where the flow of water may be easily checked. Most important

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here is to make sure the hose is not doubled or crimped to reduce the flow. This is particularly true of the slide hose.

TUBING MACHINES

Tubing machines are an important potential source of production delay and scorched stock. Although a hot die improves the surface appearance of most extruded goods, for general purposes the tubing machine should operate with as little heat as possible up to the extrusion point.

Most tubers have jacketed barrels and cored worms for cooling. Jacket temperatures can be readily determined, and if a definite increase between inlet and outlet water temperatures does not prevail, it is probably wise to clean out the jacket with the chemical cleaning solution.

As the worm heats even more rapidly than the barrel, it is essential that it be clean and that good water circulation be maintained if trouble is to be avoided. In addition to cleaning the core of the worm chemically and checking the flow of water, it is also necessary to be sure that the water is going where it does the most good. A water distributor pipe should be attached to the inlet to carry the water to the front end of the cored worm. If this pipe is badly corroded or broken off near the inlet, the cooling water does not circulate throughout the full length of the worm, and bad overheating results. If extruded stock is rough or scorches on long tubing runs, check all cooling facilities promptly.

CALENDERS

While cooling of calender rolls is important, close control of roll temperatures is a major factor in achieving a good calender job. For best results, definite roll surface temperatures, depending on the stock used and the calendering operation, are maintained by adjusting the flow of water or steam to the rolls. When the insides of calender rolls are covered with rust and scale and spray pipes are broken or clogged it is difficult and often impossible to maintain the desired roll surface temperatures. In addition, slower cooling or heating resulting from poor maintenance causes wasted time and lost production while waiting for the calender to reach the proper temperature when changing from one stock or calendering operation to another.

The length of time it takes to heat up or cool down a calender when it is in good operating condition (with clean rolls, good spray pipes, and all pipes and valves functioning properly) should be known. This can be made a matter of definite information by use of a surface pyrometer, keeping the rolls in motion while heating or cooling to avoid a lopsided temperature condition. Then the next time trouble occurs it is possible to tell whether or not some fault in the calender cooling system is causing the difficulty

Calender cooling systems may be maintained in much the same manner as mixing mill rolls. However, the rolls should be kept separated or cushioned with gum during the cleaning operation to avoid injury to the smooth machined surfaces.

It should be remembered at all times that a calender is essentially a delicate machine for fine finishing and for producing work within close tolerances. Rough surfaces due to pitting, dirt or a built-up crust of a rough material like water-glass, sometimes used to prevent sticking, makes a good calender job much more difficult to obtain.

Keep the roll surfaces clean and smooth. If the calender is to be shut down for several hours don't let cold water run through the rolls. In fact, after a

cold calender run, heat the rolls a little with steam before shutting down. This prevents moisture in the air from condensing on the surface and causing rust. If the calender is to be down for several days, coat the roll surfaces with a light oil to prevent rust. It can be easily removed with a rag and by running a little scrap stock through the calender just before using.

If the roll surfaces are fouled with dirt, make a 30–70 mixture of gum and fine (20- to 30-mesh) abrasive powder such as carborundum. Let the cold calender run at odd speed on this for an hour or two, and see what a clean, polished surface results. What is of greater importance, better looking calendered goods with less effort are obtained. Naturally a treatment of this sort does not correct warped, egg-shaped or improperly crowned calender rolls. Only new rolls or a first class grinding job rectify these troubles.

The importance of processing stocks at low temperatures was recognized with crude rubber; with the widespread use of synthetic this need has been greatly emphasized. Synthetic stocks are generally more scorchy than natural rubber stocks, and their processing temperatures are more critical. Further, the art of working away or reclaiming spoiled or partially precured synthetic stocks has not been developed to nearly the extent that it was with crude. The preferred solution is to maintain processing equipment cooling facilities to keep spoilage to a minimum.

It may not be possible at this time to install air conditioned rooms or a refrigerated water supply, but if experience is any criterion, remarkable improvement may be attained by seeing that present facilities are functioning at their best.

THE SINGLE-CORD COMPRESSION ADHESION TEST FOR EVALUATING THE ADHESION OF VULCANIZED RUBBER TO CORD *

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The replacement of natural rubber by synthetic rubberlike materials (elastomers) in the construction of mechanical goods has led to considerable emphasis being placed on the problem of strongly bonding the cord reinforcing member to these new materials. The introduction of continuous filament rayon cord as the reinforcing member in natural rubber tires had earlier given the rubber industry the opportunity to determine the importance of cord adhesion in the performance of tires. Now with the advent of synthetic, continuous filament, high polymeric materials as superior reinforcing members, the problem of adhering synthetic and natural rubber to these materials to produce satisfactory working units becomes increasingly complex.

It is evident that before very much can be accomplished with a problem of this scope a versatile test must be·devised for evaluating the adhesion of synthetic and natural rubber to the various filamentary materials. Over a period of time there has been developed in this laboratory a single-cord compression adhesion test which may be adapted to the study of the adhesion of all types of synthetic and natural vulcanized rubber to continuous or staple filamentary materials in the form of plied yarns or cord. This test is based on the fact that the apparent adhesion of cord to vulcanized rubber or rubber-like material is greatly enhanced when stripped under compression, and differences in the apparent bonding forces between different cords and different elastomers are thereby greatly magnified. The test is unique[1] in that the cord in the cylindrical adhesion test-pieces lies on a diameter at the mid-section which is stripped from the vulcanized elastomer as the ends of the test-piece are subjected to compression. In addition, the test may be performed at elevated temperatures, and is easily adaptable to routine control testing. This test seems to fill the need for a versatile, rapid and reliable adhesion test for evaluating the relative adhesion of vulcanized elastomers to cord.

EXPERIMENTAL

A. EQUIPMENT AND ACCESSORIES

Hydraulic steam press.

Drying rack for cord, 29 × 29 inches, designed to hold 26 cords 26 inches long (Figure 1, A).

Frame for aligning cord in uncured rubber block, 6 × 8 inches (Figure 1, B).

Eight one-half pound weights with clips attached (Figure 1, B and C).

Steel die, 0.70 inch internal diameter, for cutting out adhesion test-pieces (Figure 1, E).

Drill press.

Cavity mould (see Figure 2).

Oven with thermostatic control.

Open metal frame, 6×8 inches, for heating test-pieces in oven, designed to hold eight rows of seven test-pieces (Figure 1, F).

Olsen Testing Machine with compression plates and pressure indicator dial (Figure 1, G).

Miscellaneous accessories, such as shears, knife, scale, etc.
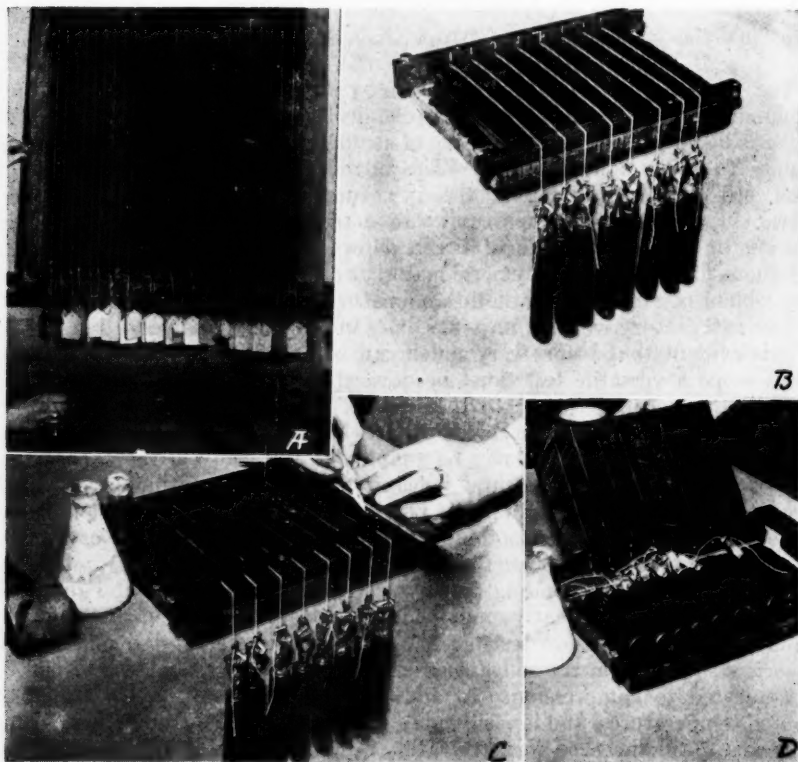
Fig. 1

B. MATERIALS

Pure-gum rubber tire carcass compound, calendered in sheets, eight inches wide and 0.25 inch thick; Olsen hardness 30 to 35; density about 0.94.

Mixture of natural rubber latex and zinc oxide for marking location of cords in the block (Figure 1, C).

Liquid soap for lubricating die (Figure 1, E).

C. TESTING PROCEDURE

I. Preparation of adhesion test-pieces

The test-pieces are usually prepared from bare and dipped cord, before and after calendering with rubber compounds. The steps in the preparation of the

test-pieces varies somewhat, depending on the purpose of the test, but the same general procedure outlined below is usually followed.

1. Uncalendered cord
   a. Untreated or bare cord

In the testing of the adhesion of the untreated cord to vulcanized elastomer, 10-inch lengths of cord are cut and placed in an oven heated to 220° F for about ten minutes immediately before placing into rubber to be cured. The
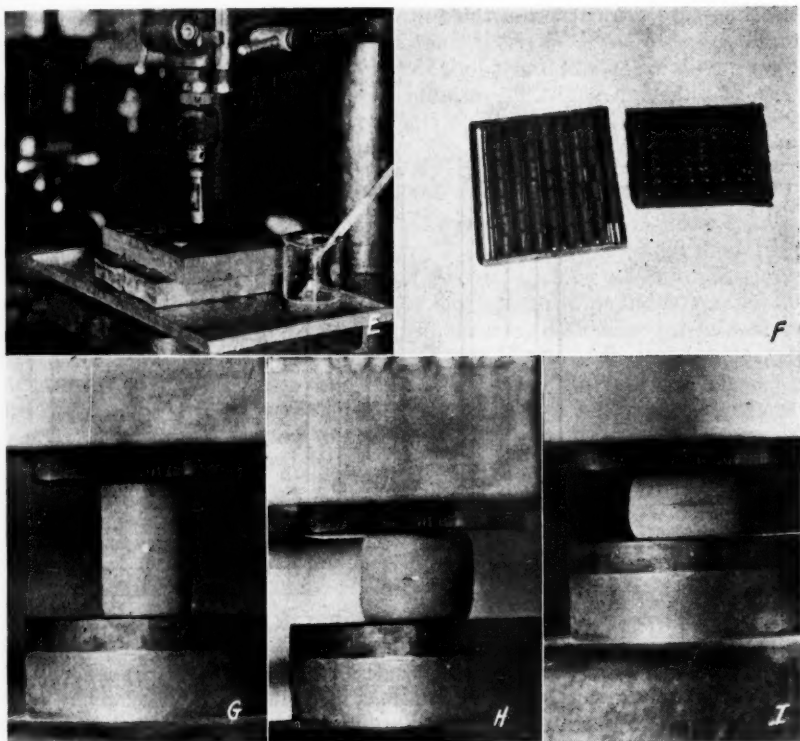
FIG. 1 continued

rubber compound having the characteristics described above is calendered into strips 8 inches wide and 0.250 inch thick. These rubber strips, usually 5 yards or more in length, are kept in rolls on racks until needed. The rubber compound should be discarded after more than six or seven days' storage under normal room conditions because its rate of cure changes with age. From the rubber strip, four pieces 6 inches wide and 8 inches long, are cut and carefully weighed. The total weight of the four pieces is adjusted so that an overflow of three to five per cent occurs during cure. For the plate mould shown in Figure 2, the total weight of the four rubber pieces is 760 grams for each cavity. Two of the rubber pieces are placed one on top of the other in the cord-block aligning frame, the dry cords fastened at one end, and spaced at one-inch

intervals across the frame (see Figure 1, B). To the free ends of the cords 0.5 pound weights are attached and allowed to hang freely. In order that the full weight may be brought to bear uniformly on the cords, the frame is tilted forward at the edge of the table after all eight lengths of cord have been securely fastened. The identification of the cords in the test-block is established by the use of the test record sheet (see Figure 3) and the relative positions of the cords in the rubber block (see Figure 1, B). The third piece of rubber is now placed precisely in place over the first two in the frame. The fourth piece of rubber is then placed over the first three. The eight cords now spaced one inch apart lie between two blocks of uncured rubber one-half inch thick. White lines are drawn across the top of the block, directly over the cords,
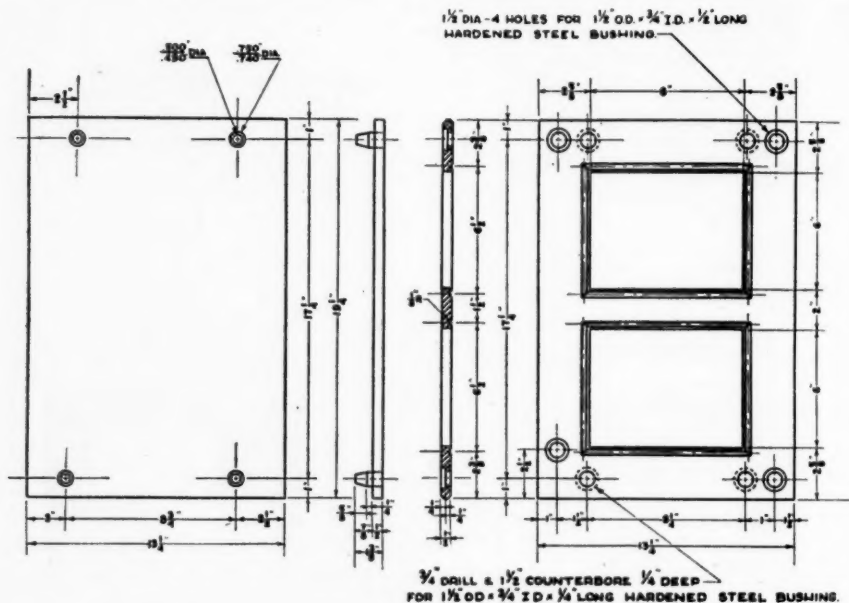
Fig. 2

using a ruler (see Figure 1, C). A mixture of 30 per cent natural rubber latex and 5 per cent zinc oxide has been found to give a permanently white line. The blade of a sharp knife is now run along the sides of the rubber block cutting the cords smoothly. The assembled block (see Figure 1, D) is then placed in the cavity mould (see Figure 2, A and B) and cured 100 minutes at 260° F under a pressure of 200 pounds per square inch. The cured rubber block is then removed from the mould and cooled to room temperature with running tap water. The block is then placed on the drill press onto which the 0.70-inch die has been fixed (see Figure 1, E) and seven test-pieces are died out along each embedded cord, using the white lines as guides (see Figure 1, F). It is important that the cord lie on a diameter of the mid-section of each 1-inch × 0.70-inch cylindrical test-piece. Each set of seven test-pieces is placed in the open metal rack in the same relative position as each occupied in the block (see Figure 1, F). The rack is then placed in an oven heated to 212° F and allowed to remain for two hours. At the end of this time the

test-pieces are removed in regular sequence according to cord number, and are tested immediately.

b. Treated cord

In determining the effect of various cord treatments on the adhesion of cord to rubber, the untreated cord is run simultaneously as a control and the increase in adhesion of the treated cord is calculated from the data obtained. The adhesive is applied to 30-inch lengths of cord, usually by dipping and, after stretching to the original length, allowed to dry on a special drying rack (see Figure 1, A). The original length of the cord is rendered certain by tying knots near the ends of the cords at fixed distances and pulling the cord back to this measured length while wet with the adhesive. The cords are allowed to air-dry at room temperature on the rack for several hours, are then removed from the rack, and are heated for ten minutes at 220° F immediately before placing in the uncured rubber. From this point the procedure is the same as that described under Section I (a) above.

c. Adhesion to various synthetic and natural rubber compounds

It is often necessary to test untreated and treated cord in more than one synthetic or natural rubber compound. This may be accomplished by an adaptation of the procedures described above, as long as the adhesion of these compounds to the pure-gum rubber block test-compound is greater than to the cord. The synthetic or natural rubber compounds are calendered into very thin sheets, 0.020 inch thick, and a strip 1 inch wide and 7 or 8 inches long is cut, folded around the cord, and pressed into intimate contact using a roller. Only one thickness of the calendered rubber, 0.020 inch, should surround uniformly the periphery of the cord at the conclusion of this operation. The overlapping edges of the calendered rubber are removed with a pair of sharp shears. The cord coated by this procedure corresponds closely to the machine-calendered cord described below. The test as modified by this procedure is designated the single-cord compression strip adhesion test.

2. Calendered cord

The procedure followed in testing the adhesion of calendered cord is essentially the same as described in Section I (a) and (b) above. A sample of calendered cord is taken either at the calender during processing or from a roll of calendered fabric. The dimensions of the sample are not important, but usually are about four inches wide by twenty-four inches long. A single cord is carefully cut from the sample with a pair of shears in such a way that the cord selected is completely encased in the calendered compound. The ten- or twelve-inch calendered cord is then knotted at one end and placed in the block-cord aligning frame as previously described. The calendered compound is seldom the same as that used in preparing the test-block proper, but must have greater adhesion to the rubber block compound than to the cord being tested, a case identical to that referred to in Section I (c) above.

II. Determination of the Apparent Adhesion

The cylindrical rubber test-pieces (Figure 1, F and G), previously heated to 212° F, are placed between the compression plates of the Olsen machine and the load is applied at the uniform rate of one inch per minute. As the test-piece is subjected to compression, the area surrounding the cord resists deformation (see Figure 1, G, H, and I) until the adhesion of the rubber to the cord

fails.   The adhesion failure is denoted by one of the dimples forming on each side of the rubber test-piece, under compression with the cord at the center, suddenly disappearing (see Figure 1, *I*). The load applied at the instant of failure is read from the Olsen pressure recording dial.   The machine should be stopped immediately, reversed to the original position, and the next test-piece substituted for the failed specimen.   The load in pounds required to cause the cord to strip from the rubber while under compression is recorded on the adhesion test record sheets (see Figure 3).   The average load required to cause

CORD ADHESION BY COMPRESSION METHOD

Test slab No. C-25
Compound No. 810
Cure: 100 min. @ 265° F
Curing: 200 lbs. per sq. in.
Date: Feb. 15, 1944

Test by John Doe
Date: Feb. 16, 1944
Tensile strength at plying $\frac{1}{2}$ lb.
Rate of compression 1 inch per min.
Specimens preheated to 212° F

	Test no.	Adhesion value		Test no.	Adhesion value
Sample 1	1	185	Sample 5	29	310
Cord Code	2	172	Cord Code	30	290
305	3	177	380	31	296
Rack No.	4	182	Rack No.	32	306
Expt. C–10	5	190	15	33	280
Req. No.	6	180	Req. No.	34	300
	7	175	10	35	294
	Ave.	180		Ave.	296
Sample 2	8	260	Sample 6	36	230
Cord Code ·	9	245	Cord Code	37	226
305	10	255	380	38	232
Rack No.	11	243	Rack No.	39	240
Expt. C–11	12	264	26	40	229
Req. No.	13	250	Req. No.	41	238
	14	238	5	42	235
	Ave.	250		Ave.	233
Sample 3	15	210	Sample 7	43	205
Cord Code	16	218	Cord Code	44	211
380	17	206	1310	45	202
Rack No.	18	220	Rack No.	46	208
Expt. C–12	19	211	57	47	200
Req. No.	20	215	Req. No.	48	216
	21	218	10	49	203
	Ave.	214		Ave.	206
Sample 4	22	241	Sample 8	50	265
Cord Code	23	236	Cord Code	51	260
380	24	250	1310	52	261
Rack No.	25	241	Rack No.	53	270
Expt. C–13	26	239	57	54	280
Req. No.	27	247	Req. No.	55	270
	28	250	7	56	250
	Ave.	243		Ave.	265

FIG. 3.—Single-cord compression adhesion test data sheet, with typical test results.

compression adhesion failure at the cord-rubber interface for the seven test-pieces is regarded as a measure of the apparent adhesion.

D. EFFECT OF TEMPERATURE ON THE COMPRESSION ADHESION OF CORD TO RUBBER

Early in the development of the single-cord compression adhesion test it was found that the apparent adhesion at the cord-rubber interface was greatly affected by the temperature of the test-piece.   In Figure 4 the results obtained
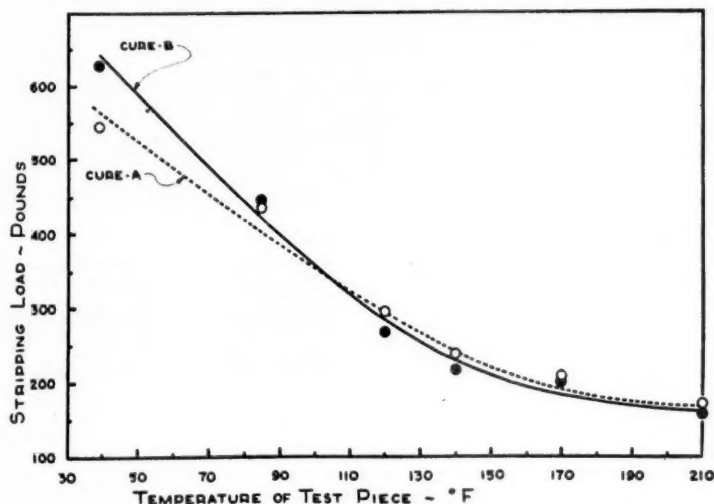

FIG. 4

by plotting the test-piece temperature against the compression stripping load for a cotton tire cord, 0.035 inch gauge, are shown.   The adhesion test-pieces were prepared as described in Section C, I, above, and heated to the temperatures indicated, beginning at room temperature, and the apparent adhesion determined as described in Section C, II.   Cure A was identical with cure B, showing the reproducibility of the results, particularly at temperatures greater than 100° F.   Since the slope of the curves approaches zero at about 200° to 212° F, this temperature range has been selected as the most desirable for routine testing when rubber compounds are used exclusively.   At this temperature, moreover, there is very little aging of the cured rubber compounds, and also the magnitude of the adhesion between cord and rubber under operating conditions can be better judged.

E. VARIATION OF THE RECORDED DATA

In a routine test, considerable reliance is placed on the average adhesion value obtained on a single test-cord.   However, when it is desired to make absolutely certain of a given adhesion value, several tests are run on the same test-cord.   Over a period of years it has been found that the coefficient of variation from test to test on the same cord, calculated from the recorded compression stripping loads, is within the range of five to ten per cent.

As a research tool the test is valuable for determining the variability of the cord adhesive as well as the variability of the adhesive film affixed to the cord. As an example, in the treatment of a continuous-filament rayon cord, 275/4/3,

with a typical natural-rubber latex adhesive, a large amount of data was collected and analyzed statistically. This analysis showed that, out of 87 tests, the average adhesion stripping load at 212° F was 229 pounds and the coefficient of variation was 13 per cent. Further calculations showed that the number of tests for a valid average on this particular system was six. Thus, if absolute certainty of a given adhesion value is desired on an adhesive of this type, at least six batches should be sampled and tested.

F. TYPES OF ADHESION FAILURES

Dissection of the individual test-pieces after failing under compression often reveals the nature of the adhesion failure. By visual inspection one may thus at times determine whether the failure occurred at (1) the rubber-adhesive interface, (2) the cord-adhesive interface, or (3) from a rubber-compound failure. The schematic drawings in Figure 5 give some idea as to
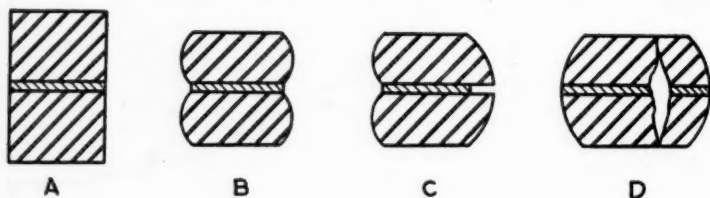

Fig. 5

the types of adhesion failures obtained when using the single-cord compression adhesion test. In A, a vertical cross-section of the original single-cord compression adhesion test-piece is shown. On application of a load the test-piece is deformed as shown in B, C represents the appearance of the test-piece at failure as typified by cases (1) and (2). In D, failure of type (3) is shown. In this latter case the adhesion failure which ordinarily begins in the center of the test-piece around the cord then migrating toward the edge is not realized, due to the cord breaking, or the rubber compound splitting to relieve the strain, or both of these events occurring simultaneously. Thus the recording of adhesion results without periodic inspection of the failed test-pieces may lead to fallacious conclusions.

DISCUSSION

At the time when the development work on the single cord compression adhesion test was initiated, cotton cord was used almost universally as the reinforcing member in mechanical rubber goods, such as, tires, belts, etc. Failure of these products in service was at times due to poor adhesion at the rubber-fabric interface, but other causes accounted for the majority of failures. For this reason the adhesion of natural-rubber to cotton-cord was considered satisfactory, and was not regarded as a major problem. However, when continuous-filament rayon cord as a reinforcing member in the construction of natural rubber tires was introduced, the importance of adhesion at the rubber-fabric interface was soon recognized. With the knowledge gained from adhesion studies on cotton cord, using the single cord compression adhesion test as a basis, specifications were established for satisfactory rayon-cord adhesion to rubber. Thus the minimum acceptable adhesion value for adhesive treated

rayon cord to a pure-gum rubber-tire carcass compound was specified as 180 pounds, by analogy with the adhesion values of 180 to 200 pounds which were usually obtained with cotton cord under the same conditions.   As long as the adhesion value of adhesive-treated rayon cord remained in the adhesion value range of cotton cord, it was found that tire performance was equal to, or better than, similar tires constructed of cotton cord.   It was found later that adhesive treated rayon cord having slightly lower adhesion values to rubber than required by the early specifications also performed satisfactorily in tires.   On the other hand it was found that, with improved adhesives for bonding rayon-cord to rubber, higher adhesion values were obtained, and tire mileage was improved in tire constructions in which adhesion failures had previously been high.   The correlation between tire performance and the adhesion values obtained using the single-cord compression adhesion test was found over a period of years covering many hundreds of tests to be exceedingly high in the rayon tire cord-natural rubber compound system.   In a similar manner, when synthetic continuous filamentary materials are processed into cords and then studied in the laboratory using the single-cord compression adhesion test as a guide, adhesion difficulties in the finished product can be reduced to a minimum or eliminated altogether.

The single-cord compression adhesion test is capable of being considerably modified without impairment of reliability.   The testing time in routine practice can be as short as seven hours.   Although an Olsen testing machine has been used in this work it is obvious that any method of applying the compression load at a uniform rate would be equally satisfactory.   The system employed of recording the adhesion values in pounds pressure can be changed to suit the individual problem.   Thus, for example, the distance which the compression-plates move before cord adhesion failure in the cylindrical test-pieces occurs expressed in linear units of measure may replace the pounds compression value.

An adhesive which is entirely satisfactory for bonding cord to elastomers at room temperature may fail completely at elevated temperatures.   Since the operating temperature of natural-rubber tires is well above 200° F, and in the case of heavy duty synthetic rubber tires may exceed 300° F, the adhesion of the cord to the elastomer at room temperature is of little importance.   As a compromise between tire-operating temperatures and room temperature, a temperature of 212° F has been found to be very satisfactory in determining the relative cord to elastomer adhesion.   It is possible that, with synthetic rubbers, higher testing temperatures may be found advantageous.

It should be clear at this point that adhesion values obtained by the single-cord compression adhesion test have no absolute meaning.   Such adhesion values are purely relative.   In reporting adhesion results it has been found convenient to record the results as percentage increases in adhesion of the adhesive-treated cord over that of the untreated cord.   Thus, for untreated rayon cord, 1100's/2, construction, 0.022-inch gauge, a compression stripping load of 80 pounds may be obtained, whereas after treating with an adhesive the failure may occur at 200 pounds for an increase of 150 per cent.   In many cases the results are simply left as an average adhesion value in pounds.   In either case, when properly designated, the experienced worker has no difficulty in recognizing the satisfactory adhesion range.

The influence of cord construction and cord gauge on the adhesion of cord to elastomers is of considerable importance.   In general it would be expected that the adhesion of a given cord material to rubber would increase as the

cord surface-area per unit length increased. There is, unfortunately, no good method for determining cord surface-area, and therefore the validity of the assumption cannot be easily proved. It has been found, however, that cord adhesion is a function of cord gauge as determined by A.S.T.M. specifications[1], all other factors remaining constant. This relationship deviates from linearity, chiefly because cord gauge is an empirical determination which defies exact mathematical expression. Nevertheless the prediction can be made with reasonable certainty that the adhesion of cord to elastomers increases with increasing cord gauge values.

The effect of cord construction on adhesion to elastomers has not been systematically investigated but, in general, the adhesion of a cord is improved as the helix angle of the cord-ply is increased with respect to the cord-axis. On the other hand, a low-density cord gives greater adhesion to elastomer than a high-density cord. Since these factors are usually opposed in the current cotton tire cord and somewhat with rayon tire cord, a balance between these factors is essential from the point of view of adhesion. Inasmuch as it is difficult to predict the effect of these factors in a given cord construction, it is well to check the cord to elastomer adhesion of all cords of new construction. The single-cord compression adhesion test has been of considerable value in this connection.

From these considerations the conclusion is drawn that, of the two recognized types of adhesion, using the terminology of McBain and others[3] of (1) mechanical, and (2) specific, the former seems to be a more apt expression in the case of cord adhesion to elastomers. Certainly in contrasting differences in adhesion of untreated cotton cord and continuous filament rayon cord, the greater adhesion of the former must be attributed to greater mechanical interlocking at the rubber-fabric interface. This conclusion is substantiated by the fact that staple rayon cord adheres to natural rubber almost as tenaciously as does cotton cord. In the case of adhesive-treated cotton and rayon cord, the mechanism of the adhesion to rubber is best explained by the mechanical concept, modified, however, in that the high-modulus cord and the low-modulus rubber are bonded by an intermediary-modulus, mutually compatible, adhesive bridge. The bonding of adhesive to cord has some of the aspects of being specific, but this is probably largely mechanical also. Credance that the "step-off" in modulus principle is responsible for the effectiveness of most cord adhesives is found in the fact that, without exception, cured films, cast from adhesives which are effective in bonding elastomers to cord, have higher moduli than elastomer compounds to which the cord is adhered. The adhesive film or material is often able to change the modulus of the elastomer compound in the vicinity of the cord by changing the state of cure, and thus a similar result of modulus gradation is obtained. Further research on this point is necessary for a definite mechanism to become established.

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THE EFFECTS OF TEMPERATURE AND HUMIDITY ON THE PHYSICAL PROPERTIES OF TIRE CORDS *

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The modern pneumatic tire is commonly classified as a rubber product. Its rubber tread satisfies the requirements of resistance to abrasion, cracks, cuts, and bruises while the rubber ply and bead stocks serve to bind its structure together into a tough, resilient unit. The rubber inner tube serves as a resilient container for the inflating air. A pneumatic tire, however, would be a flabby useless thing without the strong steel bead-wire which holds it to the wheel rim and the cord fabric which supports the major portion of the inflation stresses, but, unlike the bead wire, must also withstand repeated flexure through large amplitudes. The cord fabric, in fact, must serve in the capacity of a flexible, resilient, yet strong skeleton; resistant to heat, mechanical fatigue, and chemical attack and with a minimum of creep under sustained inflation stresses. In addition to meeting these requirements of tire service, the cord fabric must possess characteristics which permit of satisfactory processing, which may include passage through an aqueous rubber dispersion, drying at an elevated temperature, calendering, tire building, tire expansion from approximately cylindrical to toroidal form and, finally, curing in a mould at high temperature.

The foregoing brief recital of the requirements of tire cord fabric indicates the importance of properly evaluating the cord materials from the standpoint of processing and tire service. This evaluation falls naturally into three broad classifications: (1) fundamental chemical and physical studies of the base materials, (2) investigations of the properties of the various materials in cord form in relation to the various physical parameters involved in tire processing and service, and (3) determination of the optimum cord construction and treatment for each material. The discussion which follows is concerned mainly with two parameters of the second classification: temperature and moisture.

I. TENSILE PROPERTIES

SIGNIFICANCE OF THE TENSILE PROPERTIES

Tenacity and elongation, as measured with a conventional tensile testing machine, have very little direct relation to the serviceability of a tire cord. A cord of high tenacity may prove to be low in dynamic fatigue resistance; a cord showing a low "10-pound stretch" may be found to creep seriously under dead load. Still, in the majority of cases, the tensile properties may be considered as fairly reliable quality indices. Familiarity of textile and rubber technologists with measurements of this type and the simplicity of the measurements justify their employment for basic studies of cord behavior, providing no final conclusions be drawn until creep and fatigue results have been obtained. Hence, it appeared desirable to begin our studies of the effects of temperature

and moisture with tensile measurements over a wide range of temperatures and relative humidities.

The mechanism of sorption of water by cellulosic materials has been widely studied. An excellent summary of the subject is given by Valko[1].

The effects of humidity and temperature on the tensile properties of individual textile fibers and filaments have received considerable attention[2]. Wiegerink[3] devised equipment with which he determined absorbed and desorbed moisture of several types of textile yarns after treatments at various elevated temperatures and relative humidities. He found that the absorbed and desorbed water contents of variously treated cottons, and viscose, cuprammonium, and acetate rayons decreased with increasing temperature in the range of 35.5 to 150° C. He also measured changes in the tensile properties of the yarns resulting from extended conditioning at various temperatures and humidities, but the tensile measurements were made at room temperature. His results constitute a definite contribution to knowledge of the permanent effects of humidity and moisture treatments. It should be remarked, however, that Wiegerink's definition of relative humidity[4] at temperatures above 100° C appears to be incorrect. He defines relative humidity as "the ratio of the actual pressure of water vapor to the maximum possible pressure of water vapor in the atmosphere at the same temperature, expressed as a percentage". Since his conditioning chamber was at atmospheric pressure, this definition is meaningless. Busse, Lessig, Loughborough, and Larrick[5] give curves relating the "tensile strength" of cotton and rayon tire cords to temperature, measured under "oven dry" conditions, but give no data obtained at elevated humidities.

APPARATUS

A standard type X-3 Scott Tensile Machine, mounted in a room conditioned at 21.1° C and 65 per cent relative humidity was employed. A special conditioning unit, shown in Figures 1 and 2, was so constructed that it could be
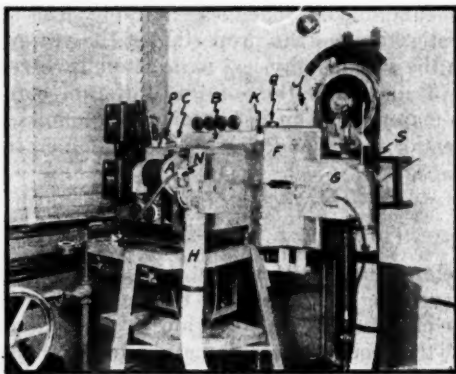

Fig. 1.—Cord humidifier—general view.

wheeled into the fabric laboratory and employed to condition the cords before and during the test, without moving the tensile machine. With the grips adjusted to test 15.4-inch cord lengths, the testing chamber G just fitted between them. Groups of 30 cords were held in clamps J and conditioned in the wide

chamber F for 1 hour before being pulled along the felt-lined slot K to the test position.   Three groups of cords could be conditioned simultaneously.   A close-up of the machine with door open is shown in Figure 2.   When a cord was actually being tested, it rode in a vertical groove, the felt lining of which barely touched the cord.   The full 15.4-inch gauge length of cord was conditioned in F but, of course, as each cord was brought to the test position and clamped around the standard grips, the ends were exposed to the conditioned room atmosphere. Then, as the test progressed (12 inches per min.), more of it was exposed at the lower end.   Thus values of elongation were obtained on a cord which was not entirely enclosed and, therefore, not strictly at the chamber temperature. However, since breaks always occurred inside the chamber, the observed break-
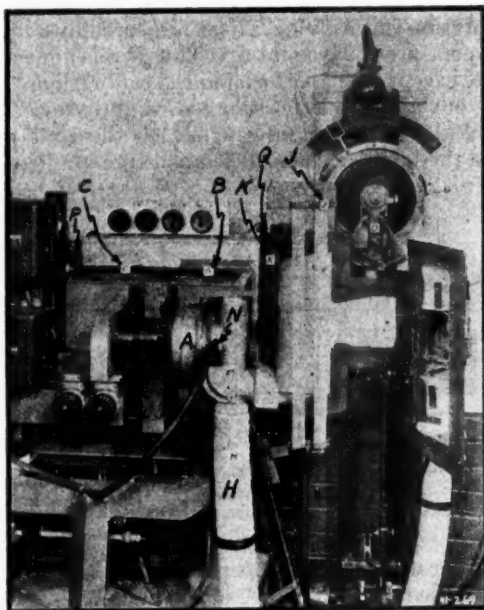
Fig. 2.—Cord humidifier—cord loading door open.

ing strengths were characteristic of the chamber temperature and humidity. Data on both tenacity and elongation are presented, but it must be remembered that the latter are only approximately correct.

The method for achieving the desired temperature and humidity in the chamber is best understood by referring to the schematic top view of Figure 3 as well as Figures 1 and 2.   Air circulation was maintained by a motor-driven blower A.   Steam injected into the air stream at N saturated the air with water vapor in a baffled compartment B.   The hot saturated air then passed into a second chamber C, where it circulated through a radiator core (from an automobile heater), which reduced the air temperature to that desired, producing saturated air at a temperature T_P, which was measured at point P.   The radiator core was maintained at the desired temperature by means of a pump-circulated water system, in which was immersed a knife heater, the current for

which was controlled with a bimetallic spiral-Mercoid relay assembly. The spiral was located at point P. To obtain regulation at lower temperatures, a cooling coil was also provided in the water system. The saturated air at temperature T_P passed next through a series of Nichrome heating elements U, where it was heated to a temperature T_Q and stirred with paddle agitators R to minimize temperature gradients before it passed over the cords in the conditioning chamber F and the cord in the testing chamber G. The temperature T_Q of the air was kept constant with another bimetallic spiral Q and Mercoid control assembly which varied the current in the Nichrome heating elements. The air finally returned to the blower through the flexible tube H. The duct system was made of Transite to as large an extent as possible to minimize heat losses and the tube H was wrapped with asbestos tape.

The temperature T_K at the cord conditioning location K was determined by means of a calibration curve giving T_K (as measured by a fine thermocouple) in terms of the temperature T_S at point S. Thus it was unnecessary to employ thermocouples at K except when performing the calibrations. The mean temperature T_G of the box at the test position was slightly lower (3 to 5° C) than T_K but, because of the short time during which the cord was at the lower temperature before the break, this small temperature gradient was ignored.
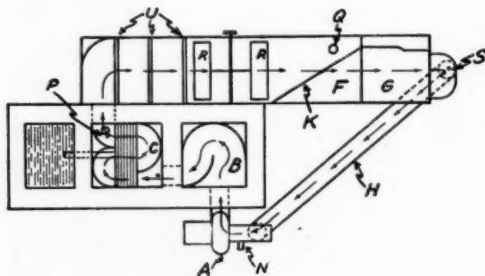

Fig. 3.—Schematic top view of cord humidifier, showing circulation path.

A dew-point psychrometer used for periodic checks of the moisture content of the air was also located at point S. A small window (not shown in Figure 1) was installed to permit observation of the polished nickel tube of the psychrometer. The tube was insulated with asbestos tape to within one inch of its lower end. The top of the tube was closed with a rubber stopper, in which were inserted a thermometer, a short glass tube extending just inside, and a long glass tube extending to the bottom of the nickel tube. The psychrometer was partially filled with ether. The short glass tube was connected to an aspirator, causing air to bubble through the ether and lower the temperature. The dew point was read by means of the thermometer immersed in the ether.

The relative humidity for any test temperature T_K was defined simply as the ratio of the density of water vapor at point K to the density of water vapor necessary to saturate the air at the conditions of point K, i.e., temperature T_K and atmospheric pressure. The density d_P of the water vapor present in the air emerging from the radiator core (at point P) was, of course, that corresponding to saturation at temperature T_P, as read from standard steam tables. As this air-water vapor mixture passed through the Nichrome heating elements, both the air and water vapor expanded according to Gay-Lussac's law. Thus,

although the ratio of water vapor to air remained constant in passing from position P to the test position K, the air was not saturated at temperature T_K obtaining at position K and the absolute humidity at K was $d_P \cdot (T_P/T_K)$, where T_P and T_K are expressed as absolute temperatures. For temperatures T_K below the boiling point of water (taken as 373° K), the density of water vapor for saturation D_K was that value given in standard steam tables, which may be denoted as D_K'. Thus, for T_K below 373° K, the relative humidity was:

$$\text{R. H.} = \frac{d_P \cdot (T_P/T_K)}{D_K'} \tag{1}$$

For T_K above 373° K, however, it was necessary to reduce the density for saturation obtained from the steam tables D_K' to the value for atmospheric pressure by means of Boyle's law. Thus, D_K became:

$$D_K = D_K' \cdot (P_O/P_K)$$

where P_O is the atmospheric pressure and P_K is the pressure of saturated vapor at temperature T_K, as read from the steam tables. Thus, for T_K above 373° K the relative humidity was calculated as:

$$\text{R. H.} = \frac{d_P \cdot (T_P/T_K)}{D_K' \cdot (P_O/P_K)} \tag{2}$$

It should be noted that this calculation ignores departures from Boyle's law. However, these departures are quite small in this range of pressures. The calculation for T_K below 373° K is essentially the same as that employed in compiling dew-point tables. Unfortunately, such tables seldom extend to temperatures above 100° C. The dew-point psychrometer at point S was employed for an additional measurement of relative humidity. The fact that values of relative humidity at point S, obtained from the psychrometer observations, agreed to within ±2 per cent with the corresponding values calculated by Expressions (1) and (2) indicates that equilibrium had been reached at the test position K and that condensation of water vapor between points P and S was negligible.

The following test procedure was employed: Cords were kept in the standard conditioned room (21.1° C, 65 per cent relative humidity) for at least 24 hours before being inserted in the special conditioning unit. Three racks of 30 cords each could be mounted simultaneously in the conditioning position K. Tensile tests were generally made on 20 cords of each group, the remaining cords being available for moisture regain measurements and emergencies. Twenty minutes was required to test a set of 20 cords. Hence, racks of 30 cords were put into the conditioning unit at 20-minute intervals, each rack being allowed to remain in the conditioning position K for 1 hour before starting the test. Thus, the average conditioning period for the cords of a given rack was 70 minutes. This period was sufficient to ensure close approach to water absorption equilibrium but was not so great as to permit large permanent changes in the cord properties. The rate at which the moisture regain (percentage moisture referred to "oven-dry" state) reached equilibrium is illustrated by Table I. The tensile measurements were performed in the usual manner except that it was necessary to use a 15.4-inch length of cord instead of the standard 10-inch length to accommodate a test chamber of reasonable dimensions between the grips. Ordinary oven-dry and conditioned tests in

TABLE I

Moisture Regain of 1100/2 Viscose Rayon Cord *vs.* Time at 150° C,
60 per cent Relative Humidity.   (Cords preconditioned 3 months at
21.1° C, 65 per cent relative humidity.)

Time at 150° C 60 per cent relative humidity (minutes)	Regain (per cent)
30	2.25
60	2.37
90	2.17
150	2.20
210	2.21

the open room were made with the 15.4-inch gauge lengths, so the results were
comparable with the tests made with cords in the special unit.   It should be
remarked that the relative humidities employed in the conditioning unit were
60 per cent or lower and the temperatures were all above 21.1° C.   The treat-
ment in the box, therefore, always involved desorption since the precondition-
ing was at 21.1° C and 65 per cent relative humidity.   In most cases, a few
cords were removed from the unit and quickly placed in weighing bottles
previously oven-dried and weighed.   The bottles were reweighed to obtain the
wet weights of the cords and then dried with stoppers out at 120° C for $1\frac{1}{2}$
hours.   The regain was then calculated as the ratio of the loss in weight of the
cord on oven-drying to its oven-dry weight.

EXPERIMENTAL RESULTS

Five different types of tire cord were chosen for this study: (1) 11/4/2
medium-stretch cotton, (2) 11/4/2 low-stretch cotton, (3) 1100/2 viscose rayon,
(4) 1100/2 Fortisan, and (5) 210/3/3 Nylon.   The resistance to rupture has
been expressed as tenacity in grams per grex[6], rather than as strength referred
to unit area to obtain a comparison of the various materials on an equal weight
basis.   The tenacity as a function of relative humidity at temperatures of 60,
100, and 150° C is given in Figures 4 and 5.   It is to be noted that the tenacity
of the low-stretch cotton cord increased much less with increasing humidity,
compared to the medium-stretch cotton.   This difference in behavior probably
resulted mainly from the fact that the low-stretch cord was much more com-
pact, and thus its tenacity was less influenced by the swelling of the cotton
fibers.   The low-stretch cotton cord probably contained somewhat more wetting
agent than the medium stretch cord, which also would tend to explain the
smaller humidity dependence of the former.   This effect must be small, how-
ever, since it was found that the two types of cotton cord had essentially the
same moisture regain.   (See Figure 12.)   It should be remembered, of course,
that the cotton fiber itself increases in tenacity with increasing humidity[7].
The commonly accepted but not too satisfactory explanation of this effect
is that the swelling by water of the less organized cellulose in the intermicellar
spaces results in an improved stress distribution and, therefore, higher tenacity
at higher humidities.   A similar explanation might be advanced for the smaller
humidity dependence of the low-stretch cotton cord for the process by which
it is produced results in a more uniform cord.   Hence the uniformizing action
of absorbed water would be expected to have a smaller effect on the tenacity of
the more uniform low-stretch cord.   The available data do not appear to be
adequate for a decision as to the relative importance of compactness and uni-
formity.   The smaller increases in tenacity observed for both types of cotton

cords at 150° C are undoubtedly the effect of the rapid decrease of moisture content between 100° C and 150° C (See Figure 12.)

The viscose-rayon cord shows the expected decrease in tenacity with increasing humidity, resulting from the swelling of the individual filaments and consequent decrease in the intermolecular forces.   The behavior of the Fortisan cord is interesting, a distinct tendency for a maximum[6] tenacity at intermediate humidities in the region of 30 per cent relative humidity appearing.   It might be said that Fortisan behaves like low-stretch cotton at the lower humidities; like rayon at higher humidities.   General considerations of the Fortisan process
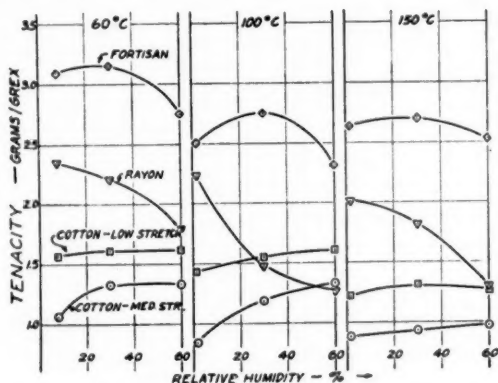

FIG. 4.—Tenacity vs. relative humidity at constant temperature—cotton, rayon, and Fortisan cords.
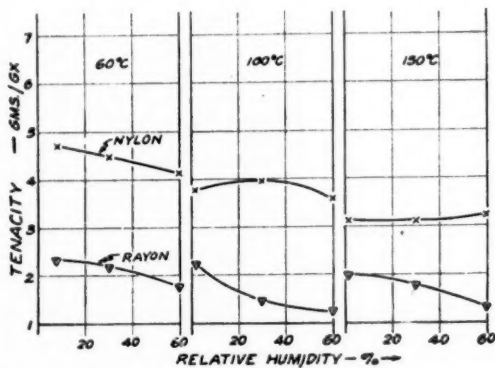
FIG. 5.—Tenacity vs. relative humidity at constant temperature—rayon and Nylon cords.

in which the cellulose is regenerated under stress from the acetate would seem to allow for a structure possessing both the discrete micellar nature of cotton and the continuous distribution of molecular weights characteristic of rayon. This rather reasonable speculation is certainly consistent with the observed behavior of the Fortisan cord.   The overall higher tenacity of Fortisan compared to rayon might result from several different factors: higher state of orientation, higher degree of polymerization, etc.

The decrease of the tenacity of the Nylon cord at 60° C (see Figure 5) is somewhat larger than might be expected from its low moisture absorption.

It might be concluded that moisture has a large effect oñ its tenacity at this temperature, since, although a smaller amount of moisture is present, the total decrease in tenacity is about as large as in the case of rayon. At the higher temperatures (100 and 150° C), the effect is smaller for Nylon, which is difficult to explain in the light of the smaller decrease of moisture content with increasing temperature found for Nylon. (See Figure 12.)

The tenacity of the cord as a function of temperature is given in Figures 6 and 7. For the oven-dry condition (relative humidity = 1.6 per cent), all
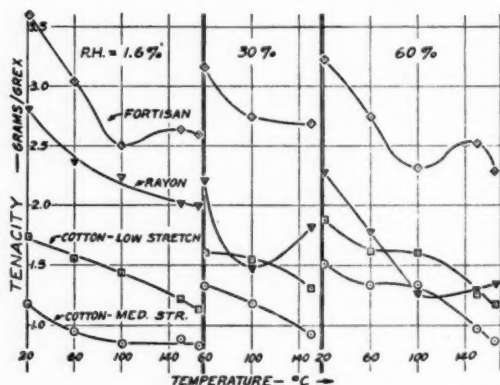
Fig. 6.—Tenacity *vs.* temperature at constant relative humidity—cotton, rayon, and Fortisan cords.
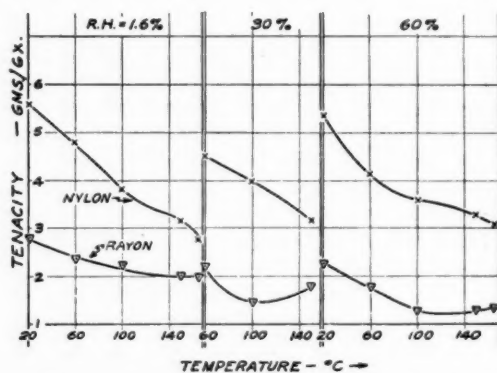
Fig. 7.—Tenacity *vs.* temperature at constant relative humidity—rayon and Nylon cords.

cords except Fortisan show the expected decrease of tenacity with increasing temperature. At relative humidities of 30 and 60 per cent, however, the tenacity of the rayon cord increases with increasing temperature in the range 100 to 150° C. The slopes of the curves for the cotton cord increase greatly in this range also. Explanations of this phenomenon will be apparent later in connection with a discussion of Figures 12 to 17.

The effects of humidity on 10-pound stretch and the ultimate stretch are given in Figures 8 and 9, respectively. In general, the extensibilities of the cords increased with increasing humidity, as is to be expected. The anomalous

minimum in the 10-pound stretch of the medium stretch cotton at 30 per cent relative humidity and 100° C is difficult to explain.   The stretch *vs.* humidity behavior of the Nylon cord is of interest since the dependence is negligible at 60° C but very large at 100 and 150° C.   It thus appears that the effect of moisture on the extensibility of Nylon is enhanced at the higher temperatures (see Figure 9) while just the opposite behavior is found for its tenacity (see Figure 5).   The close parallelism of the stretch behavior of the Fortisan and the low stretch cotton cord shown in Figures 8 to 11 is striking.   Certainly,
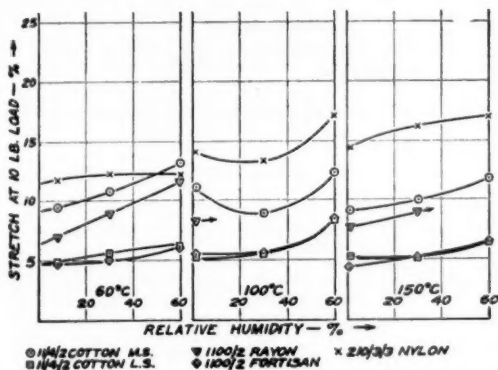
Fig. 8.—Ten-pound stretch *vs.* relative humidity at constant temperature.
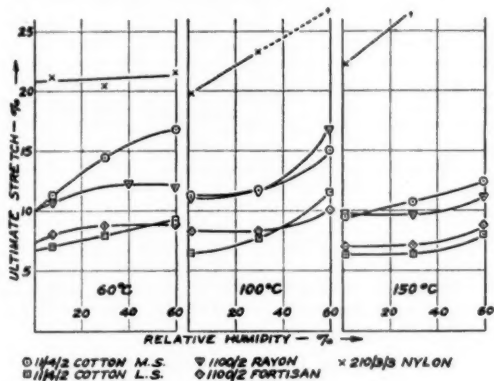
Fig. 9.—Ultimate stretch *vs.* relative humidity at constant temperature.

some of the characteristic properties of cotton have been reproduced in the Fortisan cord.   Whether this combination of the characteristics of rayon and cotton is desirable must be decided by other measurements which pertain more directly to tire service.

It should be emphasized that the temperature dependences of tenacity and extensibility at constant relative humidities of 30 and 60 per cent (see Figures 6, 7, 10, and 11) are quite misleading since the moisture content decreases rapidly with increasing temperature at a given relative humidity.   This fact is apparent from the curves of Figure 12.   Obviously, the correct method of studying the effect of temperature is to plot the tenacity and stretch against tem-
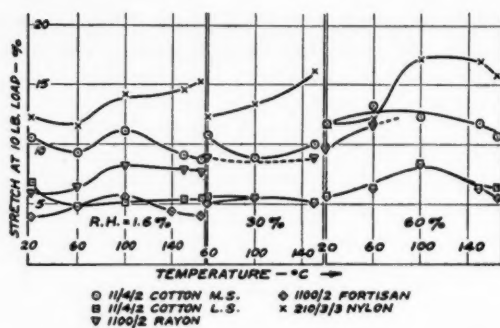
Fig. 10.—Ten-pound stretch vs. temperature at constant relative humidity.
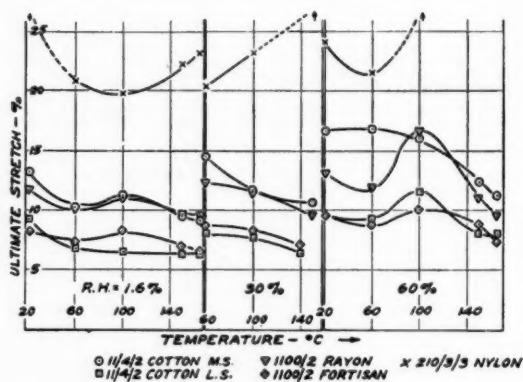
Fig. 11.—Ultimate stretch vs. temperature at constant relative humidity.
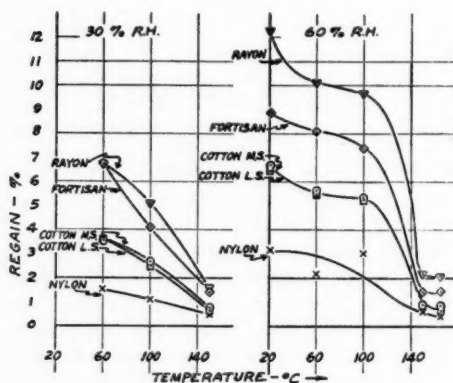
Fig. 12.—Regain vs. temperature at constant humidity.

perature for constant regain.   To obtain constant regain curves of this type, it was necessary first to plot stretch and tenacity against regain (see Figures 13 and 14) and then read the desired stretch of tenacity values at constant regain
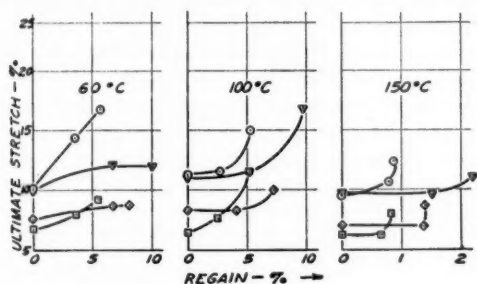
FIG. 13.—Ultimate stretch vs. regain at constant temperature.
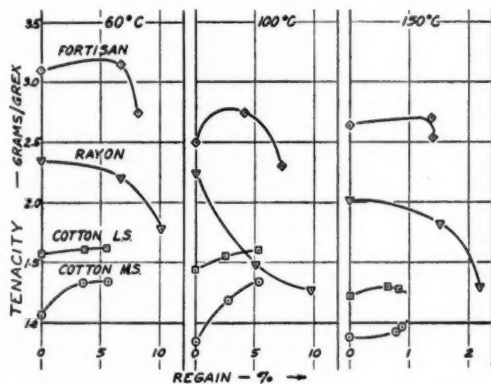
FIG. 14.—Tenacity vs. regain at constant temperature.

from the curves.   An example of the much simplified picture which is obtained by plotting tenacity vs. temperature at constant regain for the rayon cord is given in Figure 15.   Here it is clear that rayon decreases in tenacity with in-
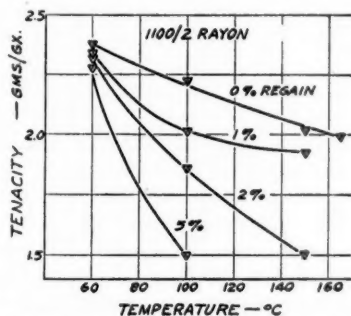
FIG. 15.—Tenacity vs. temperature at constant regain—rayon.

creasing temperature, either for the oven-dry condition or for any given moisture content. This result is of interest, since many misstatements concerning the effect of temperature on the tenacity of rayon have been made in the absence of data of this type. Certainly the well-established advantage of rayon over cotton cords in hot-running truck tires cannot be explained by these curves. However, they do suggest that rayon tires should be built in a dry state to take advantage of the high dry tenacity of rayon. This principle is well established in the tire industry after certain unfortunate experiences in the early history of rayon tire development where this precaution was not taken.

If a truck tire be built under conditions where the fabric is reasonably dry, there is every reason to suppose that the fabric will remain in a reasonably dry state, since the rate of diffusion of moisture through rubber is quite low and, in operation, the tire will run at an elevated temperature which will counteract the inward diffusion process. The problem of a passenger tire, with its relatively low operating temperature, is somewhat different, and it is quite possible that rayon might not show the advantage in a passenger tire that is found in a truck tire. This supposition is supported also by the fact that a smaller weight of rayon is generally used, compared to the cotton cord found necessary in the same size tire. In a truck tire, this reduction of weight and the correspondingly reduced thickness constitute a great advantage in increasing the rate of heat dissipation from the tire. An equivalent reduction in thickness of the passenger tire, where heat dissipation is a relatively small problem, offers only slight benefits. Thus, it may be necessary to use a greater weight of rayon cord in proportion to the cotton used in the same size passenger tire than is used in a truck tire to realize the virtues of rayon.

Curves of tenacity as a function of temperature at constant regain are given for the two types of cotton cords in Figure 16 and for Fortisan in Figure 17.
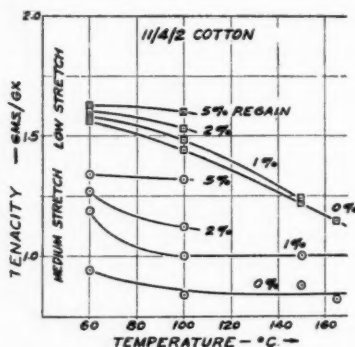
FIG. 16.—Tenacity vs. temperature at constant regain—cotton.
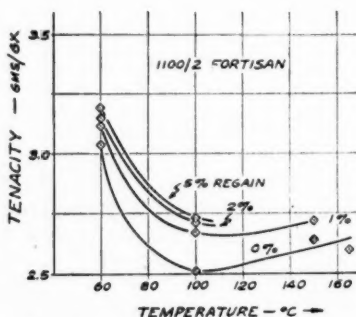
FIG. 17.—Tenacity vs. temperature at constant regain—Fortisan.

Corresponding curves have not been plotted for Nylon because of the relatively small dependence of tenacity on moisture content. The curves for cotton (Figure 16) show quite different behavior for the low and medium stretch types: The tendency of the curves to flatten out at the higher temperatures, shown for the medium-stretch cord, is absent in the case of the low-stretch cords. The much smaller dependence of tenacity on moisture regain shown by the low-stretch cotton has been attributed to its greater compactness, higher uniformity, and possibly the slightly greater wetting agent content.

Regardless of which of these factors is the most important, the rapid decrease of the tenacity of the low-stretch cord as the temperature rises above 100° C, cannot be considered favorable from the tire standpoint.   Nevertheless, the higher tenacity of the low-stretch cord compared to the medium-stretch cord, particularly for the oven-dry condition (0 per cent regain), at the higher temperatures is a point of superiority which is borne out by tire service tests.

The tenacity *vs.* temperature curves at constant regain for Fortisan show a minimum in the neighborhood of 100° C.   It appears possible that the increase of tenacity from 100 to 150° C may be explained by thermal softening of the residual cellulose acetate (probably present in a very small amount) which might result in an equalization of the internal stresses.   If the increase in tenacity in passing from 100 to 150° C be ignored, the shapes of the curves would resemble those found for medium stretch cotton.   The moisture dependence of the Fortisan is in the same direction but of smaller magnitude than that of cotton.   Thus, as mentioned earlier, the tensile properties of Fortisan appear to resemble those of cotton under some conditions; those of viscose rayon under others; and it appears possible that both the cotton and rayon types of structure may be present in Fortisan.

To indicate the changes in the stress-strain curves induced by variations in humidity and temperature, the curves of Figure 18 were reproduced from the
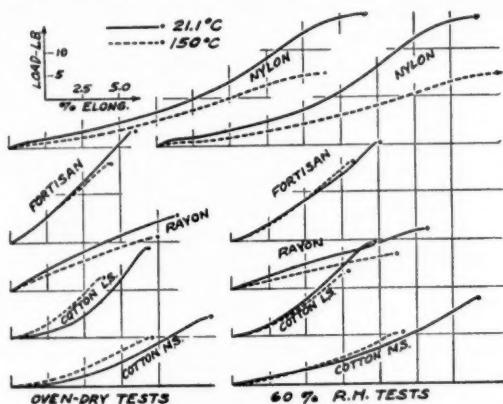
Fig. 18.—Stress-strain curves from X-3 machine.

charts actually obtained in tests with the X-3 machine, corrections being made to obtain a roughly linear scale of ordinates.   The dashed-line curves were obtained with cords at 150° C, while the full line curves refer to room temperature (21.1° C) tests.   Two sets of curves are given for oven-dry and 60 per cent relative humidity conditions, respectively.   While the general behavior of the cord is summarized by these curves, it must be remembered that they do not accurately portray the stress-strain relation for reasons known to those who have employed the constant rate of stretch type of tensile machine.   Unfortunately, the inclined plane tester, which yields more reliable stress-strain curves, was not of convenient construction for use with the conditioning chamber.

It should be remarked that the oven-dry results at room temperature were obtained by the conventional procedure, where the cords were dried in an oven at 100° C for 1 hour; then removed singly and tested in the atmosphere of the

testing room (21.1° C, 65 per cent relative humidity) as quickly as possible after removal. Thus, there are two points of uncertainty in the room temperature oven-dry results: (1) Did the cords reach 21.1° C in the 15 seconds elapsing between removal and break, and (2) was appreciable moisture absorbed in this period? To investigate point (1), fine (No. 40 B. and S.) iron-constantan thermocouple junctions were inserted at the centers of 3-ply cotton and rayon cords, and the temperature *vs.* time curves during the oven-dry testing operations were obtained with a rapid recording potentiometer (Weston model 721). These curves are shown in Figure 19. It is clear that the temperatures at the
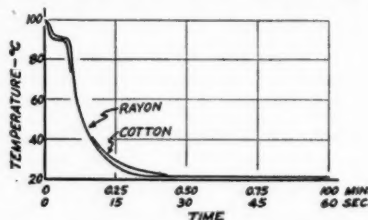
Fig. 19.—Cooling curves of three-ply cotton and rayon cords removed from oven into conditioned room.

centers of the cords dropped to within 5° C of the testing room temperature at 15 seconds after removal from the drying oven. Thus, the break occurred with the cord at approximately 21.1° C. Nevertheless, during the early part of the stressing, the cords were at higher temperatures, which condition may have slightly influenced the breaking elongations and, therefore, the tenacities. The possibility (2) was studied by measuring the dependence of moisture regain on time after removal from the oven (see Figure 20). About 1.0 per cent
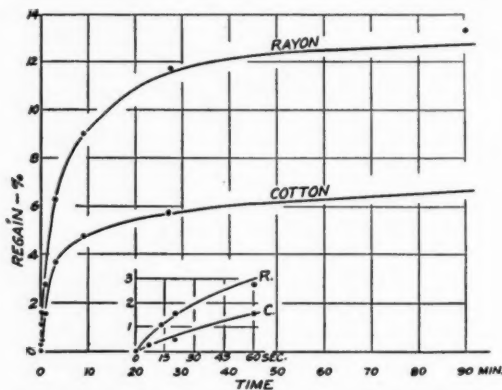
Fig. 20.—Regain curves of three-ply cotton and rayon cords removed from oven into conditioned room.

moisture was absorbed in the 15 seconds interval in the case of rayon and 0.5 per cent for cotton. Thus, the room temperature oven-dry values of the tenacity were probably slightly high for the cotton and slightly low for rayon. However, these errors would be rather small, so the essential qualitative arguments drawn from Figure 6 would not be invalidated. The presence of these uncertainties suggests, nevertheless, that a true oven-dry test at room temperature should be developed.

II. CREEP CHARACTERISTICS

SIGNIFICANCE OF CREEP

Any segment of a cord in a tire in service bears a static inflation load of 1 to 3 pounds on which is superposed a dynamic load which varies with the speed and the location of the cord segment in the tire.   While the dynamic load undoubtedly affects the amount of creep of the cord to some extent, it appears reasonable to assume that the static load is the predominant factor.   Because of the seriousness of the "growth" of tires over long periods of service, then, it was decided to make a study of the creep of the same cords employed in the tensile experiments of Part I, over a range of static loads and temperatures.

APPARATUS

The creep apparatus shown in Figure 21 was essentially an insulated constant temperature box in which 20-inch lengths of cords were hung, the top
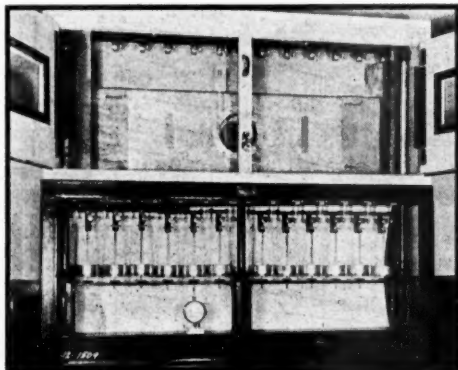
FIG. 21.—Cord creep apparatus.

grips were inside the box, but the grips attached to the weight pans, which were prevented from rotation by means of guide studs, were just below and outside the box.   A counterbalanced dial gauge, equipped with an accurately machined base, rested on the accurate stationary steel bar below the weight pans.   Thus, the dial gauge could be moved successively to positions below each of the 12 loaded cords in the box and the vertical position of each weight could be measured as a function of time.   Neglecting the short length of cord which emerged below the box as the test progressed, the elongation increment, defined as the additional elongation occurring after 0.002 hour, was calculated from the differences in dial gauge readings at time t and 0.002 hour, respectively. The initial length in all the calculations was taken as 20 inches under a "straightening load" of 1 ounce.   The origin of creep times was selected as 0.002 hour for the reason that measurements seldom could be made at shorter times than 0.002 hour after applying the loads.   The cords were heated for 10 minutes after the thermometer reached the desired temperature, but before applying the loads, to insure uniform temperatures throughout the box and within the cords.

To obtain an approximate figure for the absolute elongation of each cord at 0.002 hour after loading, an India ink mark was made at a point on the cord

just outside the box, one minute after applying the 1-ounce load.   The distance between the top grip and the bottom of the box was known and, hence, the initial length and the length at some later time when the creep rate was conveniently low could be measured.   Comparison of these values with the corresponding dial gauge readings gave the absolute elongation where desired. It seemed preferable, however, to include the inherent inaccuracies of this type of measurement to as small an extent as possible in the creep results. Hence, the relatively more accurate elongation increment was used in plotting the creep curves and the absolute elongation at 0.002 hour was calculated as a separate index to express approximately the extent of the rapid deformation occurring previous to that time.

EXPERIMENTAL RESULTS

The elongation increment is plotted against logarithmic time in Figures 22 to 26.   The creep curves for the two types of cotton cords (Figures 22 and 23)
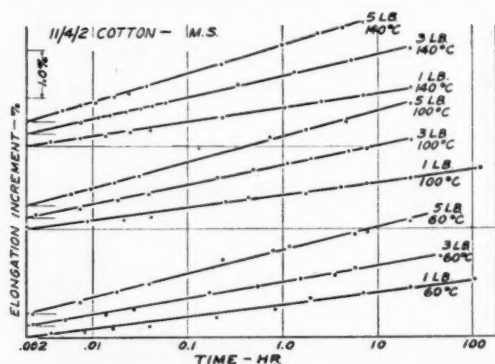
FIG. 22.—Elongation increment vs. logarithmic time—cotton MS.
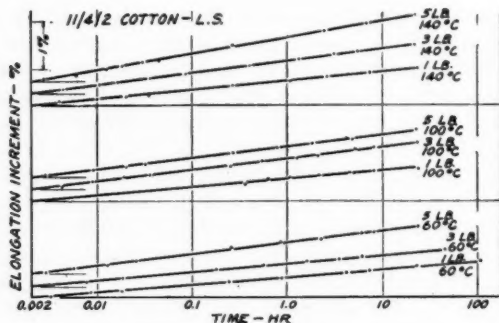
FIG. 23.—Elongation increment vs. logarithmic time—cotton LS.

are seen to be linear in the time period investigated.   The dependence of the slope S on load is seen to be of the type expected, although S does not increase proportionally to load.   The slope increases with increasing temperature, suggesting that creep takes place within the individual cotton fibers to a con-
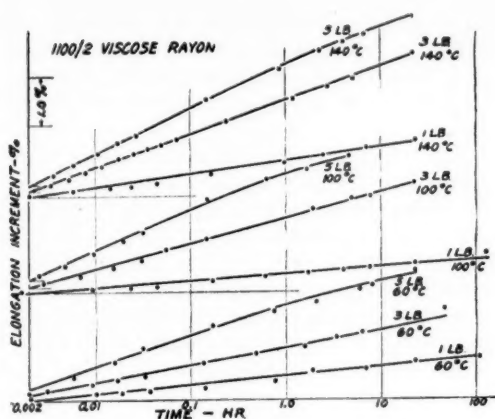
Fig. 24.—Elongation increment vs. logarithmic time—rayon.
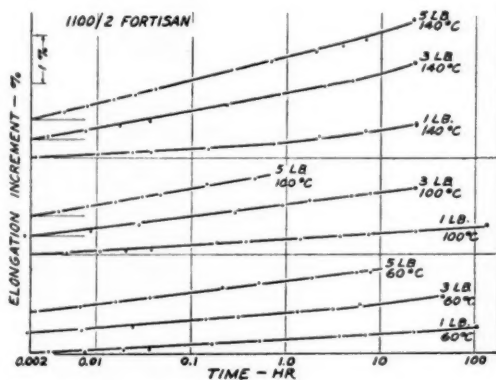
Fig. 25.—Elongation increment vs. logarithmic time—Fortisan.
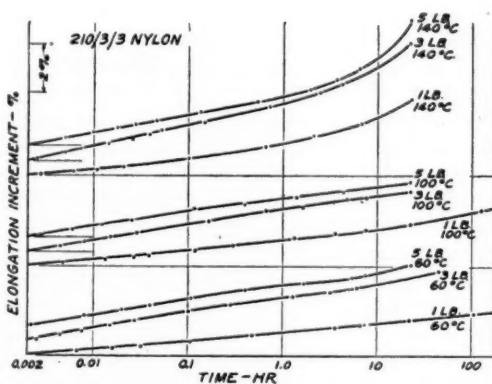
Fig. 26.—Elongation increment vs. logarithmic time—Nylon.

siderable extent. It is evident also that the rate of creep, as measured by the slope S, is lower for the low-stretch cotton cord, consistent with its lower 10-pound stretch. It should be remarked that the low-stretch cotton cord was considerably lighter (4950 grex) compared to the medium-stretch cord (5580 grex).

The creep curves for the rayon cord (Figure 24) show a tendency to decrease in slope for times longer than 1 hour at the highest load (5 pounds). In this respect, the curves differ from those published by Busse, Lessig, Loughborough and Larrick[5], where a distinct increase in slope was shown. However, the cords employed in that work were of different construction (275/4/3), and most of the curves presented were for temperatures of 150° C or higher. Hence, the two sets of data are not strictly comparable. At the higher loads, the creep of the rayon cord (Figure 24), was much greater than that for either of the cotton cords. On the other hand, the rayon cord was much lighter (2660 grex) than the low stretch cotton cord (4950 grex). Thus, the creep at 3-pound load for the rayon cords may be roughly compared with that at 5-pound load for the low stretch cotton. On this equal weight basis, the rayon cord still appears to creep more rapidly than the low stretch cotton, in keeping with the known greater growth of rayon tires. To make a more exact comparison, of course, the creep loads chosen for cotton and rayon, respectively, should be equal to the inflation loads for individual cords in tires, as built (not on an equal weight basis).

The Fortisan cord (2920 grex) appears to creep considerably less than rayon (2660 grex) at the higher temperatures and loads and a slight tendency for the slope to increase is apparent (Figure 25). This tendency is much greater for Nylon (Figure 26), which shows considerable departures from linearity, suggesting that chemical degradation takes place at the higher temperatures. Nylon also exhibits anomalous behavior as regards the dependences of creep on load and temperature. For Nylon, and possibly to a lesser extent for the other materials, it appears that the initial elongation e_0 must be taken into account as well as the slope S.

To compare both the initial elongation and the slope of the creep curves on an equal weight basis, two arbitrary indices were defined: initial compliance $= e_0/P =$ elongation at 0.002 hour divided by the unit load P in grams per grex; weighted creep $= S/P =$ slope of logarithmic creep curve divided by the unit load P in grams per grex. It should be noted that the slope S is the change in the elongation increment in the period t_1 to t_2 divided by $\log(t_2/t_1)$.

These indices were calculated at the 5-pound load for the two cotton cords and at the 3-pound load for the others, in order that the comparison would be at approximately the same "unit load" (load/lineal weight of cord). This procedure was desirable since the slope vs. load relation was not linear. The data are summarized in this form in Table II at temperatures of 100 and 140° C. The 60° C data were omitted, since they were subject to errors from moisture effects. As previously judged, from casual examination of the creep curves, rayon appears to have a much higher creep than that of low-stretch cotton, although the initial compliance is much lower. Fortisan appears comparable to low-stretch cotton in creep, but much stiffer from the view-point of initial compliance. Nylon has about the same creep as that of rayon, but is much softer in initial compliance. It must be remembered, of course, that the figures for the slope S are based on the early linear portions of the creep curves. Thus, the values of S/P for Nylon given in Table II must be considered minimum

TABLE II

WEIGHTED CREEP S/P AND INITIAL COMPLIANCE e_0/P

Temp. (°C)	Index	M.S. cotton	L.S. cotton	Rayon	Fortisan	Nylon
100	e_0/P	20.8	14.1	2.9	5.1	10.4
	S/P	1.3	0.52	1.0	0.48	1.0
140	e_0/P	24.6	14.3	5.0	5.6	14.0
	S/P	1.5	0.74	1.3	0.71	1.5

Note: Both indices expressed as per cent grex/gram.

figures, for the slope S increases at the longer times of creep. Because of the nonlinear dependence of S on load and the uncertainty concerning the constancy of S at extended creep times, it is clear that these laboratory creep measurements must be considered only as qualitative indications of the creep characteristics, as related to tire growth. It is interesting that the creep curves for cords of viscose rayon and Nylon are of same general type found for single filaments of viscose rayon and Nylon by Leaderman[8].

SUMMARY

It may be concluded from the foregoing experiments that measurements of tenacity and stretch at a single relative humidity have little meaning, since the important variable, moisture content, decreases rapidly with increasing temperature. The most revealing representation of tenacity or elongation appears to be as a function of temperature at constant moisture regain. Curves of this type show that the tenacity of a modern viscose rayon cord decreases with increasing temperature in the range of regains 0–5 per cent. The same general behavior is exhibited by low-stretch cotton cord, but the tenacity vs. temperature curves for medium-stretch cotton cord flatten off at temperatures above 100° C. The tenacity of Fortisan cord decreases rapidly with temperature up to 100° C, and then increases slightly between 100° and 165° C. Nylon cord shows a rapid decrease of tenacity with increasing temperature, but maintains its advantage in tenacity over that of rayon for all temperatures and humidities included in these experiments.

For any given temperature, increase of moisture content increases the tenacity of the cotton cords to an extent dependent on the "stretch" of the cord; decreases the tenacity of rayon cord. Fortisan increases in tanacity with increasing moisture content in the lower range of moisture contents (like cotton) and then decreases in tenacity for higher moisture contents (like rayon). The tenacity of Nylon decreases very slightly with increasing moisture content.

All of the cord materials investigated, cotton, rayon, Fortisan, and Nylon, increase in stretch (10-pound or ultimate) as the moisture content increases. The effect of temperature at constant regain on stretch, however, is rather complicated. Until a method of measuring stretch with the whole cord continuously within the testing chamber is devised, further conclusions would be unjustified.

Analyses of the creep characteristics of the various cord materials on the basis of two arbitrarily defined indices "initial compliance" and "weighted creep" yield several basic facts: The low-stretch cotton cord exhibits lower values of both indices compared to medium-stretch cotton, as might be anticipated from tensile measurements. The rayon cord, however, has a much lower "initial compliance" but a definitely higher "weighted creep," compared

to the low-stretch cotton. The Fortisan cord is comparable in "weighted creep" to low-stretch cotton, but has a much lower "initial compliance". The Nylon cord has an "initial compliance" approaching that of low stretch cotton, but a much higher "weighted creep", which is equal to or greater than that of rayon. The elongation increment *vs.* logarithmic time curves for cotton, rayon, and Fortisan are very nearly linear over the period 0.002–20 hour, but those for Nylon show a tendency to increase in slope at times beyond 1 hour.

In conclusion, it may be said that the results of these experiments agree very well with current concepts of the structures of cotton, rayon, and Nylon, and have rather interesting implications in regard to the structure of Fortisan. It is well to remember that a complete evaluation of a tire cord should include dynamic fatigue measurements as well as tensile and creep data. The complicated nature of the fatigue problem, however, necessitates an extended separate discussion which is beyond the scope of this paper.

ACKNOWLEDGMENT

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CONTROL OF ELONGATION IN HIGHLY STRETCHED COTTON TIRE CORD*

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INTRODUCTION

The useful life of a pneumatic tire is known to depend to a large degree on the quality of the cord used in its manufacture. Quality is not a simple function of any one measurable property, but rather a combination of a multitude of properties. Just what the contribution of some of the individual properties is, or what constitutes the best combination of properties, is not completely understood. This study is primarily concerned with only two properties: (1) the breaking strength and (2) the elongation[1] at a load of ten pounds, and with methods for their improvement and control.

Many efforts have been directed toward the improvement of cord strength because, other things being equal, the stronger cord will make the better tire. Most of the methods that have been described for the improvement of cord strength are stretching treatments. As early as 1930, Sessions[2] described a treatment by which the dry tire cord was stretched with or without the application of heat and pressure during the stretching. The use of a rubberizing bath during stretching was contemplated, but no water was employed. Brownell[3] improved the strength of very highly twisted tire cord by applying a stretching treatment to the plied yarns as well as to the whole cord. The stretching was carried out with or without previous wetting of the cord, but no heat was applied during or after the stretching. He stated that a cord which was passed through a liquid before the stretching had a greater strength and lower elongation than one merely stretched in the dry state. Gwaltney, Graybill, and Newton[4] patented a process for the manufacture of heat-resistant tire cord, in which the plied yarns were saturated with a liquid and then either wet-twisted under a tension just short of the breaking point, or wet-twisted in the usual manner, after which the finished wet cord was stretched under a tension short of the breaking point. They, too, did not contemplate the use of heat during the stretching, but reported an even greater strength and lower elongation when the wet cord was compressed by passing it through a nipper after the stretching.

A treatment used to improve the strength of sewing thread by wetting and stretching without heat is reported by Burgeni[5]. The process is similar to the tire cord treatment of Brownell, as well as that of Gwaltney, Graybill, and Newton.

Nickerson[6] obtained an Australian patent for a method of improving the strength of tire cord by wetting it, then stretching and while under tension heating it by means of moist or dry heat. He obtained improvements in bone-

dry strength of about 45 per cent with elongations at 10 pounds as low as 2 to 3 per cent. Nickerson observed that the strength was directly, and the elongation inversely, proportional to the tension used. He stated that no additional benefits were gained by giving cord repeated stretching treatments under identical conditions.

Most tire manufacturers agree that cord which has too much stretch permits an undesirable permanent enlargement of the tires during use, known as "tire growth". Too little stretch in the cord will impair the impact strength of tires; i.e., they will not be able to withstand the sudden shocks caused by stones and irregularities of the road. There is no general agreement as to what the optimum elongation is, but some tire manufacturers consider an elongation of around 6 per cent at 10 pounds, measured under bone-dry conditions, as most desirable for cotton cord. In this investigation, the range of 6 to 6.5 per cent was considered to be the optimum. Of course, the stretch characteristics of tire cord are fully represented only by a load-elongation curve; but as long as the general shape of this curve remains the same, the elongation at a particular load is a fair measure of the stretch properties of the cord.

The elongation of tire cords which have been treated by any of the known stretching methods is always much lower than that of untreated cords. When cord is stretched to such a degree as to give it the greatest possible strength, its elongation at 10 pounds is usually well below the optimum range. There is a definite reciprocal relationship between the strength and elongation of stretched tire cords. As a result, one has the choice of producing either very strong cords, of very low elongation, or cords of optimum elongation, with comparatively slight improvement in strength. The two properties, strength and elongation, are thus linked together in such a manner that it has seemed impossible to take full advantage of any of the stretching treatments. Part of the potential strength obtainable by stretching had to be sacrificed to keep the elongation at 10 pounds within an acceptable range. Strength and elongation could not be controlled independently.

Recently, however, our efforts to produce a tire cord that would combine almost maximum strength with optimum elongation have led to the development of a dual-stretching treatment which permits a control of the elongation to be realized almost independently of the improvement in the strength of the cord.

MATERIALS AND METHODS

All the tire cords used in this investigation were made on conventional machines in the experimental cotton mill at the Southern Regional Research Laboratory. Several different cotton varieties and cord constructions were used in the experiments to make sure that the observed effects were not restricted to any one cotton or construction. The cottons used, together with their staple lengths, were as follows:

Stoneville 2B	$1\frac{3}{32}$ inches
Delfos 651	$1\frac{1}{8}$ inches
Acala 1517	$1\frac{5}{32}$ inches
Wilds 13	$1\frac{11}{32}$ inches
$S \times P$	$1\frac{1}{2}$ inches

Treated and untreated cords were tested for tensile strength and for elongation at 10 pounds on a Scott tire-cord tester equipped with ink recording device, in conformity with specifications for testing tire cord of the American Society

for Testing Materials, Committee D-13 on Textile Materials[7], with the exception that ten breaks only were made for most samples and that the tests were made under "bone-dry" conditions instead of standard conditions of temperature and humidity.   Bone-dry conditions were selected so that the results could be more readily compared with those obtained by other laboratories which maintain different atmospheric conditions.   To have the samples bone-dry, a bundle of cords, consisting of a few more than ten pieces cut to a suitable length and held together loosely by a cord bearing an identification tag, was placed with one end slightly protruding in an open wide-mouthed bottle. The bottle was placed in an electric, forced-draft oven, thermostatically controlled at 225° F.   After two and one-half hours the bottle was removed from the oven and a wad of cotton was pushed into the top in such a way that one end of the bundle of test-pieces remained outside, permitting the pieces to be pulled out individually for testing.   Ten breaks were finished in about five minutes, so that almost no trend could be observed in the strength and elongation data caused by absorption of moisture from the air during testing.   The elongations were read from the autographic load-elongation charts obtained by the Scott tire-cord tester.   Where gauge or count measurements are given, they were taken under standard atmospheric conditions of 70° F and 65 per cent relative humidity.

The various stretching treatments were carried out on a small, laboratory-scale stretching apparatus, similar to that used by Nickerson[6], which was especially adapted for the purpose at hand.   Figure 1 shows a schematic drawing of this apparatus.
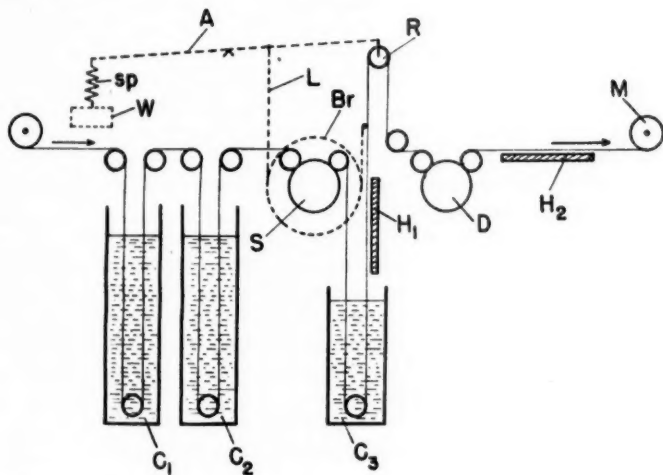
Fig. 1.—Laboratory-scale stretching apparatus. C_1, C_2, C_3, liquid containers; S, snub rolls; D, driving rolls; Br, brake roll; M, winding spool; R, small roll; A, lever arm; L, leather belt; sp, spring; W, weight; H_1, H_2, electric hot plates.

The cord was allowed to pass through the two containers C_1 and C_2, which were filled with a swelling agent for cellulose.   As such, plain water was used, or water containing a wetting agent, which accelerated penetration of the cord and thereby hastened the swelling action.   The cord was then stretched under constant tension between the snub rolls S and the driving rolls D by a mecha-

nism indicated by the dotted lines in Figure 1.   This tensioning device consisted of a small roll R over which the cord had to pass on its way from the snub rolls to the driving rolls and which was attached to the lever arm A.   The lever arm carried a weight W suspended by means of a spring sp on the other end and could act on the snub rolls S by way of the leather belt L laid around the brake roll Br which, in turn, was mounted on the same shaft as the snub roll S.   The spring sp acted as a shock absorber, and greatly improved the smoothness of operation of the mechanism.   The only motor-driven parts in the whole apparatus were the driving roll D and the roll M onto which the treated cord was wound.   Between the driving rolls D and the winding roll M the cord was under only negligible tension.

The snub rolls S were driven by the cord itself, but they could only turn if the grip which the leather belt had on the brake roll was released by a downward movement of the small roll R, thus creating a tension in the cord which could be controlled by the size of the weight W.   If, because of irregularities, some parts of the cord stretched more than preceding parts, then the small roll R moved upwards, thereby slowing up the snub rolls until the predetermined tension was set up in the cord again.   If a part of the cord did not stretch sufficiently, the roll R was pulled down to such an extent as to speed up the snub rolls until equilibrium was reëstablished.   It was thus possible to stretch cord at any predetermined constant load.   While under tension, the cord could be wetted again by a liquid contained in C_3.

If it was desired to apply heat during or after the stretching an electric hotplate, twelve inches long, could be placed either at H_1 or at H_2.   In the position H_1 heat was applied to the cord under tension.   In the position H_2 the heater merely served as a drier, since the rolls M and D moved at about the same surface speed, and consequently the cord was under no tension at H_2.   The temperature of the hot plate could be regulated by means of a variable transformer.   The surface temperature was selected so that it would completely dry the cord without damaging it; this depended on the gauge of the cord and the speed at which it passed over the heater.   At the slow speed at which this particular stretching apparatus was operated (about 143 yards per hour) the surface temperature of the hot plate was between 320 and 360° F.

It appeared from experiments, using several variations of the machine described, that the particular type of stretching mechanism used does not affect the results in general, although it may have an influence on the uniformity of the product.   Thus, two sets of rolls driven at different speed, or two sets of rolls of different diameter driven at the same speed, or a pair of capstans were also found satisfactory for stretching the cord.   In place of the electric heater, infrared radiation proved adequate.

EXPERIMENTS AND RESULTS

STRETCHING UNDER VARIOUS CONDITIONS OF MOISTURE AND HEAT

To find the best combination of factors known to improve the strength of tire cord, various treatments involving one stretching under various conditions of moisture, heat, and tension were investigated.   The following are representative of the results obtained.   In one experiment a tire cord, made from $S \times P$ cotton and having a 21/5/3 construction, was simply stretched in the apparatus after the manner of the Sessions method[2], without any liquid being in the three containers, in the absence of any heat, and with the greatest tension possible

without breakage.   In this instance the applied tension could not exceed 15 pounds.   As will be seen from Table I, rows 1 and 2, the strength of this "dry-

TABLE I

INFLUENCE OF VARIOUS STRETCHING TREATMENTS ON STRENGTH, AND ON ELONGATION AT 10 POUNDS OF 21/5/3 TIRE CORDS MADE FROM DIFFERENT COTTONS

Cotton variety	Treatment	Cord gauge (in.)	Bone-dry strength (lb.)	Strength based on control (per cent)	Bone-dry elongation at 10 lb. (per cent)
(1) $S \times P$	Control	0.034	20.0	100.0	8.2
(2) $S \times P$	Dry-stretching	0.031	25.6	128.0	4.4
(3) Acala	Control	0.033	15.7	100.0	9.4
(4) Acala	Cold-wet-stretching	0.030	20.0	127.4	6.8
(5) Stoneville $2B$	Control	0.034	16.2	100.0	9.4
(6) Stoneville $2B$	Steam-stretching	0.030	20.7	127.8	5.7
(7) Acala	Control	0.033	15.7	100.0	9.4
(8) Acala	Hot-wet-stretching	0.029	23.3	148.4	4.6

stretched" cord was increased by about 28 per cent as the result of this treatment, while the cord's gauge and its elongation at 10 pounds were reduced, the latter well below the optimum range.   When lower tensions were used for stretching, the elongation could be brought up to 6 to 6.5 per cent, but the strength increase was very small.

In another single-stretching experiment, employing 21/5/3 tire cord made from Acala cotton, the three containers C_1, C_2 and C_3, through which the cord had to pass before being stretched at a tension just short of the breaking point (13 pounds), were filled with ordinary water.   Again no heat was applied to the cord under tension, but the cord was dried over the electric hot-plate at H_2, when it was no longer under tension.   The only difference between this and the preceding experiment is that in this one the cord was stretched in a wet condition, as contemplated in the Brownell patent[3].   Since no heat was employed while the cord was under tension, this treatment will be referred to as "cold-wet-stretching".   The results of the tests, given in Table I, rows 3 and 4, show that this treatment gave about the same relative increase in strength and decrease in gauge, but that the elongation was not reduced to below the optimum range.   A further reduction in elongation was impossible because the cord broke if greater tension was used.   Almost identical results (not shown) were obtained by this treatment, omitting use of the hot plate in position H_2.

Next, the effect of a "steam-stretching" treatment on a 21/5/3 tire cord made from Stoneville $2B$ cotton was tried.   Before being stretched at maximum tension (14 pounds), the cord was passed through a glass tube, 10 inches long and of $\frac{1}{4}$-inch inside diameter, which was placed between the container C_2 and the snub rolls S (see Figure 1).   Saturated steam was blown through the tube, entering through a sidearm located midway between the ends.   The three containers were empty.   Again no heat was applied while the cord was being stretched, but at times a heater was placed at H_2 without having any influence on the results obtained.   The testing results given in Table I, rows 5 and 6, show that the effects of this treatment on gauge, strength, and elongation were about the same as those of the two single-stretching treatments previously described.   The elongation was reduced to a value below the optimum and

could be increased only by use of a lower tension which greatly reduced the strength of the treated cord.

Finally, a single-stretching treatment, which consisted of the combined application of water, tension, and heat according to the method described by Nickerson[6], was applied to the same 21/5/3 cord as was employed for the cold-wet-stretching experiment (Acala cotton). In this experiment the experimental conditions were almost the same as for the cold-wet-stretching treatment reported in row 4 of Table I, the only exception being that the heater was placed at H_1 instead of H_2 so that heat was applied to the moistened and stretched cord while under tension. The cord was wetted by passing through the two containers, C_1 and C_2, filled with water; was stretched just short of the breaking point (11 pounds) between the snub rolls S and the driving rolls D; and was exposed to heat, while under tension, at H_1. This treatment, which will be referred to as "hot-wet-stretching", gave the results shown in Table I, rows 7 and 8. The relative strength increase amounted to about 48 per cent, while gauge and elongation again showed a pronounced decrease. This same treatment, applied to the 21/5/3 cords made from the $S \times P$ and Stoneville 2B cottons, gave strength increases of 53 per cent and 40 per cent, respectively.

The greatest strength increase was thus obtained by the "hot-wet-stretching" treatment. It is important to point out the difference between this and the "cold-wet-stretching" treatment. Heat was employed in both processes. However, while it served merely as a means of drying in the cold-wet-stretching treatment, it was an essential part of the process in the hot-wet-stretching treatment. This is evidenced by the facts that the strength and elongation at 10 pounds of a cold-wet-stretched tire cord were not influenced by the use or nonuse of heat after the stretching, whereas, when heat was omitted during the hot-wet-stretching treatment, only a little more than half as much strength increase was obtained. Fundamentally, hot-wet-stretching consists of the simultaneous application of moisture, heat, and tension, while cold-wet-stretching employs only moisture and tension.

INFLUENCE OF AMOUNT OF TENSION DURING HOT-WET-STRETCHING

To determine the influence of amount of tension employed during hot-wet-stretching, a tire cord of 29/5/3 construction, made from Wilds 13 cotton, was passed through water and then, while under different tensions, over the heater placed at position H_1 in Figure 1. Thus, all the cords in this series were treated alike—i.e., they were moistened, stretched, and heated while in the stretched condition—except for the amount of tension used for the stretching. The results, presented in Table II, clearly demonstrate a reciprocal relationship

TABLE II

INFLUENCE OF TENSION DURING HOT-WET-STRETCHING ON STRENGTH AND ELONGATION OF A 29/5/3 TIRE CORD MADE FROM WILDS 13 COTTON

Treatment	Tension (lb.)	Bone-dry strength (lb.)	Strength based on control (per cent)	Bone-dry elongation at 10 lb. (per cent)
Untreated	—	15.5	100.0	8.8
Hot-wet-stretched	1.5	16.8	108.4	5.6
Hot-wet-stretched	2.5	17.4	112.3	5.1
Hot-wet-stretched	4.5	17.8	114.8	4.8
Hot-wet-stretched	8.5	20.7	133.5	4.2
Hot-wet-stretched	10.5	20.8	134.2	3.9

between strength and elongation of cords subjected to the hot-wet-stretching treatment. As the tension employed during the stretching was increased, the treated cord became stronger, but its subsequent elongation at 10 pounds became smaller. The load-elongation curves, obtained on the Scott tire-cord tester, and from which the data of Table II were taken, are shown as broken
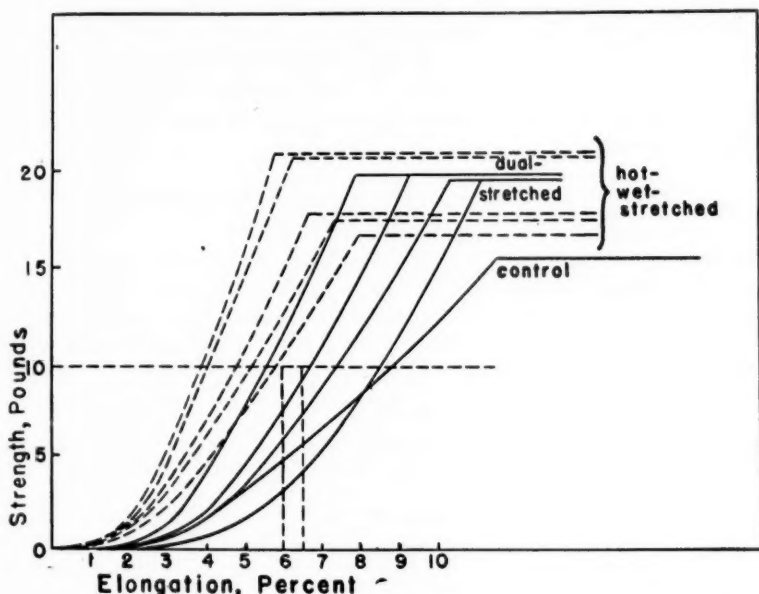
FIG. 2.—Load-elongation curves of variously treated 29/5/3 tire cords made from Wilds 13 cotton. Broken lines for cords hot-wet-stretched with tension, reading from left to right, of 10.5, 8.5, 4.5, 2.5, and 1.5 pounds. Continuous lines (except control) for cords dual-stretched with 10.5 pounds tension during the first phase and, reading from left to right, with 6.5, 3.5, 0.5, and 0 pounds tension during second phase.

lines in Figure 2. In general, the observations recorded in Table II and Figure 2 apply to the other single-stretching treatments as well.

INFLUENCE OF TIME OF SWELLING BEFORE HOT-WET-STRETCHING

Another factor found to have an influence, mainly on the elongation at 10 pounds, is the degree of swelling of the cotton cord before being exposed to tension and heat. This is shown by an experiment with samples of a 29/5/3 tire cord, made from Acala cotton, which were all stretched and heated under the same tension ($9\frac{1}{2}$ pounds) by the heater in position H_1 but, before the stretching, were swollen to varying degrees by adjusting the level of water in C_1 and C_2. The time during which the cords were exposed to water varied from 2 to 60 seconds and was used as a measure of their degree of swelling. From the results of this experiment, given in Table III, the time of swelling had an inconsequential influence on the strength of the treated cord, but there was a tendency toward higher elongation with increasing degree of swelling. This effect was also observed when a wetting agent was added to the water instead of increasing the time of swelling. Thus, variation of the degree of swelling permits a very limited control of elongation independently of the strength;

TABLE III

INFLUENCE OF TIME OF SWELLING BEFORE HOT-WET-STRETCHING ON STRENGTH AND ELONGATION OF A 29/5/3 TIRE CORD MADE FROM ACALA COTTON

Time of swelling (seconds)	Bone-dry strength (lb.)	Bone-dry elongation at 10 lb. (per cent)
2	17.3	4.1
14	17.6	4.2
36	17.5	4.5
60	18.2	4.7

however, in most cases this control is insufficient to bring the elongation up into the optimum range.

INFLUENCE OF WATER OF VARIOUS TEMPERATURES ON HOT-WET-STRETCHED CORD

When a 29/5/3 tire cord (made from Wilds 13 cotton), which had been strengthened about 38 per cent by hot-wet-stretching, was cut into 10-yard pieces and immersed in water of selected temperatures for 3 minutes, and then air-dried, these pieces were found to have increased elongation, regardless of the temperature of the water used (see Table IV), and in some cases the elonga-

TABLE IV

INFLUENCE OF WATER OF VARIOUS TEMPERATURES ON STRENGTH AND ELONGATION OF HOT-WET-STRETCHED 29/5/3 TIRE CORD MADE FROM WILDS 13 COTTON

Treatment	Temperature of water (degrees C)	Bone-dry strength (lb.)	Strength based on control (per cent)	Bone-dry elongation at 10 lb. (per cent)
Untreated control	—	15.5	100.0	8.8
Hot-wet-stretched	—	21.4	138.1	4.0
As above, then water 3 min.	15	19.8	127.7	8.0
As above, then water 3 min.	25	19.6	126.5	8.4
As above, then water 30 min.	25	19.0	122.5	9.8
As above, then water 3 min.	35	19.3	124.5	9.8
As above, then water 3 min.	50	19.4	125.2	10.4
As above, then water 3 min.	75	19.2	123.9	10.4
As above, then water 3 min.	100	19.5	125.8	8.7

tion exceeded that of the untreated control cord. The strength, however, remained about 26 per cent greater than it was before the application of the stretching treatment, which means that in this particular case almost 70 per cent of the improvement was retained even after 3 minutes' exposure to boiling water. The cord was almost as strong after 30 minutes' exposure to water of room temperature. Stretching the cord in the presence of water and heat and subsequently exposing it to water thus produced a cord which had about the same elongation at 10 pounds but considerably more strength, when compared to the untreated cord.

CONTROL OF ELONGATION BY DUAL STRETCHING

The observation on the effect of water on hot-wet-stretched cord suggested a method which for the first time makes possible improvement in the strength of tire cord without reducing its elongation at 10 pounds below the optimum value. Obviously, it was only necessary to decrease the elongation of an

already strengthened and relaxed cord. For this purpose, a second wet-stretching treatment was considered to be logical. Therefore, a 29/5/3 tire cord (made from Wilds 13 cotton) was first hot-wet-stretched in the stretching apparatus with the heater position at H_1 (see Figure 1). The cord was then allowed to travel a second time through the two water-filled containers, C_1 and C_2, after which it was stretched between S and D in the absence of heat and dried over a hot plate at position H_2. This treatment will be referred to as the "dual stretching" process. Four samples were prepared, each under a different tension during the second stretching, as shown in Table V. (In the treatment at zero tension the hot-wet-stretched cord was immersed in water for 3 minutes and then allowed to air-dry.)

TABLE V

INFLUENCE OF TENSION DURING SECOND PHASE OF DUAL STRETCHING ON STRENGTH AND ELONGATION OF A 29/5/3 TIRE CORD MADE FROM WILDS 13 COTTON

	Tension during				Bone-dry
Treatment	1st stretch- ing (lb.)	2nd stretch- ing (lb.)	Bone-dry strength (lb.)	Strength based on control (per cent)	elonga- tion at 10 lb. (per cent)
Untreated control	—	—	15.5	100.0	8.8
Hot-wet-stretched	10.5	—	20.8	134.2	3.9
Dual stretched	10.5	6.5	19.8	127.7	5.7
Dual stretched	10.5	3.5	19.8	127.7	6.8
Dual stretched	10.5	0.5	19.4	125.2	7.5
Dual stretched	10.5	0	19.6	126.5	8.4

It will be seen from Table V that when a single hot-wet-stretching treatment was employed, using a tension of 10.5 pounds and the heater at H_1, an increase of some 34 per cent in strength over the control was obtained but the elongation at 10 pounds was reduced to 3.9 per cent. When this treatment was followed by a second hot-wet-stretching, the elongation remained unchanged. When parts of the once hot-wet-stretched cord were stretched a second time with the heater at H_2 and with tensions ranging from 6.5 to 0.5 pounds, elongations at 10 pounds of 5.7 to 7.5 per cent were obtained. With tensions greater than 6.5 pounds, elongations down to 3.9 per cent could be produced in this cord, and with smaller tensions than 0.5 pound up to 8.4 per cent. At the same time Table V shows that the strength retained in the dual-stretched cord is independent of the tension applied during the second stretching treatment and about 27 per cent higher than that of the control. These conditions are also demonstrated by Figure 2, in which the load-elongation curves of these dual-stretched cords, as obtained on the Scott tire-cord tester, are shown as continuous. This means that the second stretching treatment maintained almost 80 per cent of the increase in strength achieved by the first stretching treatment, while it permitted adjustment of elongation at 10 pounds to any value between that of the control and that of the hot-wet-stretched cord. In many cases it has been possible to maintain an even higher percentage of the maximum potential strength of the cord, as will be seen later (Table VII).

INFLUENCE OF SWELLING TIME BEFORE SECOND PHASE OF DUAL STRETCHING

A 23/4/3 tire cord, made from Stoneville 2B cotton, was first hot-wet-stretched at a tension of 8.5 pounds, with the heater at H_1. This prestretched

cord was then cut into several lengths, each of which was cold-wet-stretched at a tension of 10.5 pounds, with the heater at H_2 for drying after release of tension. The only variable during the second stretching was the time of swelling, which was again controlled by the proper adjustment of the water level in containers C_1 and C_2, the speed of the machine being constant. The results of strength and elongation measurements given in Table VI, when compared with

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TABLE VI

INFLUENCE OF TIME OF SWELLING BEFORE SECOND PART OF DUAL STRETCHING ON STRENGTH AND ELONGATION OF A 23/4/3 TIRE CORD MADE FROM STONEVILLE 2B COTTON

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Time of swelling (seconds)	Bone-dry strength (lb.)	Bone-dry elongation at 10 lb. (per cent)
2	17.7	4.7
12	16.9	5.3
60	17.1	6.3

those in Table III, show that the influence of the time of swelling before the second stretching is considerably more pronounced than before the first stretching. The strength, however, does not appear to be affected by the time of swelling.

APPLICATION OF DUAL-STRETCHING TREATMENT

With proper selection and control of tension and degree of swelling during the second stretching, the dual-stretching treatment was applied to a number of cotton cords of different construction, gauge, and cotton variety. The procedure employed for the preparation of these cords consisted in passing them through water containing a wetting agent (Aerosol OT), applying the highest tension that could be used without breaking them, and heating them while under this tension. The maximum tension that could be applied safely was, roughly, about 68 per cent of the average bone-dry strength of the untreated cord. Small portions of each hot-wet-stretched cord were then restretched under various conditions of swelling and tension to determine the proper conditions for optimum elongation. Guided by these preliminary trials, the remaining portion of each cord was stretched, and the properties of the dual-stretched cord were measured. The results are presented in Table VII, the unstretched controls being identified by c, the hot-wet-stretched cords by h, and the dual-stretched by d. Some of the cords listed in Table VII represent lots of 1000 yards; most of them represent only 200 yards.

According to Table VII the strength increase for the hot-wet-stretching treatment ranged from about 39 to 63 per cent, while the other single-stretching treatments did not improve the strength by more than 28 per cent (Table I). The improvement in strength was accompanied by a reduction in gauge and an increase in yarn number or count. If the strength is expressed as count-strength product or in grams per denier, either of which takes account of the simultaneous change in yarn number and strength, the hot-wet-stretching treatment gave increases ranging from 48 to 83 per cent for the thirteen cords listed in Table VII. The strengths of the dual-stretched cords were from 25 to 48 per cent higher than those of the untreated samples (Table VII); or, expressed as count-strength product or in grams per denier, the increase varied

TABLE VII
PROPERTIES OF UNSTRETCHED, HOT-WET-STRETCHED AND DUAL-STRETCHED TIRE CORDS MADE FROM DIFFERENT COTTONS

Cotton variety	Construc- tion	Treat- ment*	Gauge (in.)	Yarn No.	Bone-dry strength (lb.)	Strength based on control (per cent)	Bone-dry elonga- tion at 10 lb. (per cent)
Stoneville 2B	29/5/3	c	0.029	1.56	12.0	100.0	9.9
Stoneville 2B	29/5/3	h	0.025	1.78	17.0	141.7	4.1
Stoneville 2B	29/5/3	d	0.026	1.72	15.8	131.7	6.0
Acala	29/5/3	c	0.028	1.64	12.4	100.0	10.2
Acala	29/5/3	h	0.025	1.81	16.6	133.9	5.6
Acala	29/5/3	d	0.025	1.79	16.4	132.2	6.0
Delfos	29/5/3	c	0.028	1.60	12.3	100.0	10.2
Delfos	29/5/3	h	0.025	1.77	17.4	141.5	5.1
Delfos	29/5/3	d	0.025	1.71	16.7	135.8	6.4
Wilds 13	29/5/3	c	0.028	1.54	15.5	100.0	10.0
Wilds 13	29/5/3	h	0.026	1.75	21.6	139.4	4.4
Wilds 13	29/5/3	d	0.026	1.65	19.4	125.2	6.6
$S \times P$	29/5/3	c	0.029	1.59	15.0	100.0	10.3
$S \times P$	29/5/3	h	0.025	1.81	20.5	136.7	5.7
$S \times P$	29/5/3	d	0.025	1.80	19.6	130.7	6.7
Stoneville 2B	23/4/3	c	0.030	1.52	12.6	100.0	9.2
Stoneville 2B	23/4/3	h	0.026	1.69	17.5	138.9	5.2
Stoneville 2B	23/4/3	d	0.027	1.67	17.1	135.7	6.2
Acala	23/4/3	c	0.029	1.52	12.0	100.0	10.6
Acala	23/4/3	h	0.026	1.67	16.8	140.0	5.2
Acala	23/4/3	d	0.026	1.69	16.0	133.3	6.3
Delfos	23/4/3	c	0.029	1.49	13.4	100.0	10.2
Delfos	23/4/3	h	0.026	1.68	19.4	144.8	5.0
Delfos	23/4/3	d	0.026	1.66	17.7	132.1	6.0
Wilds 13	23/4/3	c	0.029	1.50	14.4	100.0	9.9
Wilds 13	23/4/3	h	0.026	1.69	20.8	144.4	4.8
Wilds 13	23/4/3	d	0.026	1.68	20.2	140.3	5.9
$S \times P$	23/4/3	c	0.029	1.53	14.8	100.0	9.9
$S \times P$	23/4/3	h	0.026	1.71	21.7	146.6	4.7
$S \times P$	23/4/3	d	0.025	1.68	21.4	144.6	6.2
Wilds 13	17/4/3	c	0.033	1.12	19.2	100.0	10.2
Wilds 13	17/4/3	h	0.029	1.27	29.2	152.1	4.4
Wilds 13	17/4/3	d	0.030	1.27	27.1	141.1	6.4
Stoneville 2B	21/5/3	c	0.034	1.15	15.8	100.0	9.2
Stoneville 2B	21/5/3	h	0.029	1.29	25.8	163.3	4.3
Stoneville 2B	21/5/3	d	0.030	1.31	23.3	147.5	6.2
Acala	20/5/3	c	0.035	1.05	17.3	100.0	11.6
Acala	20/5/3	h	0.030	1.27	26.0	150.3	4.3
Acala	20/5/3	d	0.031	1.21	23.6	136.4	6.7

* c = untreated control; h = hot-wet-stretched; d = dual-stretched.

from 34 to 68 per cent for different cords. On the average, 93 per cent of the count-strength product obtained by the hot-wet-stretching treatment was retained after the second stretching.

DISCUSSION OF RESULTS

The hot-wet-stretching treatment, involving the combined application of tension and heat to the swollen cord, gave considerably greater strength than other single-stretching treatments employing various combinations of tension, moisture, and steam. However, the main difficulty involved in this as well as in the other single-stretching treatments is the reciprocal relationship between strength and elongation, as illustrated by Table II. In the case of the 29/5/3 cord reported in this table, a tension of 10.5 pounds produced a cord having a strength 34 per cent greater than that of the control but an elongation of only 3.9 per cent at 10 pounds, which is definitely too low for tire cord. The elongation could be maintained at 5.6 per cent or above by using a tension of 1.5 pounds or less, but such a low tension yielded a cord only 8.4 per cent stronger than the control. This reciprocal relationship prevents the full utilization of the potential strength of the cord and thus limits the practical usefulness of this and similar single stretching treatments.

The cold-wet-stretching treatment recorded in Table I, rows 3 and 4, had the advantage of not reducing the elongation as much as did the other single-stretching treatments, but it too did not permit independent control of the elongation. With any of these treatments a compromise between optimum elongation and maximum strength would have to be accepted.

In this respect, the advantage of the dual-stretching treatment over the single-stretching treatment is at once evident. This is demonstrated by Figure 2, which shows the influence of tension on strength and elongation of both hot-wet-stretched and dual-stretched cords, and also by comparison of Tables II and V. When the tension used in the preparation of hot-wet-stretched 29/5/3 cord from Wilds 13 cotton was decreased (Table II), the elongation became greater but at the same time the strength declined until, at a tension of 1.5 pounds, the strength was only 8.4 per cent greater than that of the control and the elongation was 5.6 per cent, which was still short of the optimum. When, however, the tension during the second phase of the dual-stretching treatment was lowered (Table V), the elongation at 10 pounds was increased up to that of the control, while the strength remained independent of the elongation. The proper tension for yielding optimum elongation can easily be determined, and the strength of the dual-stretched cord will be about 27 per cent greater than that of the control, regardless of the choice of elongation. By single stretching a strength increase of about 27 per cent could be obtained for this cord only if an elongation at 10 pounds of between 4.2 and 4.6 per cent were accepted.

The dual-stretching treatment thus makes possible the production of a tire cord having greatly improved strength, and a predetermined, independently controlled elongation at 10 pounds between that obtainable by the hot-wet-stretching treatment and that of the untreated cord, or even a little higher than the latter. In the case of the thirteen cords for which data are given in Table VII, the average count-strength product of the dual-stretched cords was only about 7 per cent lower than the maximum obtainable by hot-wet-stretching, and the elongation at 10 pounds of each of the dual-stretched cords was either within or very close to the optimum range of 6 to 6.5 per cent.

Different cords showed different response to the single as well as to the double-stretching treatment. It can be expected that the twist and the construction of the cord will be important factors in determining how much improvement in strength is obtainable by any stretching treatment. Most

important of all, however, appeared to be the uniformity of the cord. Cords of high uniformity could be subjected to relatively higher tensions during stretching and consequently their relative increase of strength, after stretching under maximum tension, was greater. Cords with weak spots or "riders" (cork-screw) showed the least benefit from the treatment; the 29/5/3 Acala cord in Table VII is an example of such a non-uniform cord.

The dual-stretching treatment does not seem to offer any difficulties that would impede commercial application, although the experiments thus far have been restricted to small, laboratory-scale production. The treatment consists of two phases which, however, can easily be combined into one continuous process by proper design of the stretching machine. During the first phase the cord is given possibly the greatest strength that can be attained, without regard to elongation. This is accomplished by wetting the cord, stretching it under a tension just short of the breaking point, and heating it while under tension. During the second phase, the cord is wetted again and stretched at a predetermined tension in the absence of heat, but is dried without tension just before it is wound on a spool. This phase gives the cord the desired elongation at 10 pounds while retaining approximately 93 per cent of the maximum count-strength product obtained during the first phase. The proper tension for the second stretching is determined by a few preliminary trials on short pieces of cord. If the desired elongation should lie outside of the range of elongations obtainable by variation of tension, a further adjustment is possible by varying the degree of swelling. This can be done by adding a wetting agent to the water through which the cord travels or by changing the time during which the cord is exposed to the swelling action of water in the second phase. Thus, in the dual-stretching treatment a method has been found to control effectively the elongation of highly stretched and strengthened tire cord.

SUMMARY

1. Cotton tire cords, differing with regard to gauge, construction, and variety of cotton, were subjected to stretching treatments involving various combinations of tension, heat, and moisture. It was found that all these treatments increased the strength of the cords but reduced their gauge and elongation at 10 pounds. The greatest increase in strength was obtained when tire cord was stretched in a swollen condition and in the presence of heat. Increases in count-strength product from 48 to 83 per cent were observed.

2. Experiments showed a reciprocal relationship between the strength and the elongation at 10 pounds obtainable by single-stretching treatments of tire cord, which makes impossible the control of elongation, independently of strength. Bone-dry elongations of about 6 per cent at 10 pounds could be obtained only with negligible increase in strength.

3. The original elongation was restored by treating highly stretched tire cord with water at room temperature for 30 minutes or with boiling water for 3 minutes, while most of the increase in strength resulting from stretching was retained. A hot-wet-stretched tire cord after treating with water had equal elongation but greater strength as compared with the untreated cord.

4. A dual-stretching method was devised which makes possible the control of elongation at 10 pounds independently of strength. The treatment consists of two phases: the first imparts to the cord the maximum potential breaking strength and the second serves to adjust the elongation at 10 pounds to a predetermined controlled value while maintaining over 90 per cent of the maxi-

mum count-strength product. Control of the elongation is achieved by proper selection of tension and degree of swelling during the second phase of the dual-stretching treatment.

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REFERENCES

[1] Elongation is to be understood as the deformation in the direction of load caused by a tensile force, in accordance with the definition under D12–42 of A.S.T.M. Committee D-13 on Textile Materials (see Reference 7). It is expressed as a percentage of the original length.

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